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THE HEAT OF FORMATION OF WATER

By Frederick D. Rossini

ABSTRACT

The usually accepted value for the heat of formation of water is based upon measurements made by Thomsen in 1873, Schuller and Wartha in 1877, and Mixter in 1903. The most reliable of these data are those of Schuller and Wartha, whose average value has an uncertainty of some 8 parts in 10,000, practically all of which lies in the calibration factor of their calorimeter.

The procedure employed in the present investigation was to determine directly the quantitative correspondence between the energy liberated by (1) the reaction of hydrogen and oxygen to form a weighed mass of liquid H_2O and (2) a measured quantity of electrical energy, using the calorimeter as the absorber of the two quantities of energy and its temperature rise as the comparator. In so far as systematic errors are concerned, the absolute accuracy of the result obtained by this substitution method depends principally upon the determination of the mass of water formed, in grams, and of the quantity of electrical energy, in terms of the mean solar second and the international volt and international ohm as maintained at this bureau. High precision was obtained by the use of proper calorimetric technic, a sensitive device for measuring changes of temperature, a sensitive potentiometric system for measuring the electrical power input, a precise timing device, and a suitable balance for weighing the H_2O formed.

The data of two sets, each including the results of nine experiments, give for the heat of formation of liquid H_2O, at 25° C. and a constant pressure of 1 atmosphere, 285,775 international joules per mole (18.0156 g). The estimated uncertainty in this value is ± 40 joules. With the factors 1.0004 and $\frac{1.0004}{4.185}$, this value is equivalent to 285,890 absolute joules and to 68,313 g cal_{15}. The maximum and the average deviations of the experiments, in per cent, are, respectively, 0.031 and 0.019 in Set I; 0.024 and 0.010 in Set II.

The data of Schuller and Wartha, Thomsen, and Mixter, recomputed in terms of the international joule, are in substantial agreement with the value obtained in the present investigation.

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I. INTRODUCTION

The heat of formation of water is one of the most important constants in thermochemistry because it is involved directly in the calculation of the heats of formation of practically all organic and of many inorganic compounds.

The thermal energy liberated when hydrogen and oxygen gases combine to form water has been measured by many investigators. Of the 14 papers dealing with this problem during the past century, the first appeared in 1828 and the last in 1907.[1] The various experiments were performed under widely different conditions. Some involved combustion by explosion in a bomb at constant volume, while others were made by burning one of the gases in an atmosphere of the other at constant pressure. The reaction temperatures employed by the different investigators ranged from 0° C. to room temperature. The errors of measurement were much less for the investigators who worked after about 1860 than for their predecessors, because of the development of better measuring devices and technic. However, even in the case of the most reliable of these experiments, those of Schuller and Wartha in 1877, an uncertainty of about 8 parts in 10,000 still exists.[2]

With the great increase in accuracy and precision of calorimetric measuring instruments, methods, and devices, and with the facilities available for calibration and standardization at this bureau, it was felt that the uncertainty in the value selected for the heat of formation of water could be reduced to 1 or 2 parts in 10,000.

II. METHOD

The method employed in this investigation was as follows: The apparatus consisted of a calorimeter surrounded by a constant temperature jacket. The calorimeter was composed of a calorimeter can containing a weighed mass of water, a device for measuring changes of temperature, a stirring mechanism, a reaction vessel for burning the gases at constant pressure, and a heating coil. The problem was to determine the quantitative correspondence between the thermal energy liberated by (1) the reaction of hydrogen and oxygen to form a weighed mass of liquid H_2O, and (2) a measured quantity of electrical energy, using the calorimeter as the absorber of the two quantities of energy and its temperature rise as the comparator. A combustion experiment, in which a mass of m grams of water was formed in the reaction vessel, produced a temperature rise of Δt degrees in

[1] These papers, as compiled by F. R. Bichowsky in the International Critical Tables, **5,** pages 176, 207–211, are listed in chronological order:
(*a*) Despretz, Annales de chimie et de physique, **37,** p. 180; 1828.
(*b*) Dulong, Comptes rendus, **7,** p. 871; 1838.
(*c*) Grassi, Journal de pharmacie et de chimie, **8,** p. 170; 1845.
(*d*) Abria, Comptes rendus, **22,** p. 372; 1846.
(*e*) Favre and Silbermann, Comptes rendus, **23,** p. 411; 1846.
(*f*) Andrews, Philosophical Magazine, **32,** p. 321; 1848.
(*g*) Thomsen, Annalen der Physik und Chemie, **148,** p. 368; 1873.
(*h*) von Than, Berichte, **10,** p. 947; 1877.
(*i*) Schuller and Wertha, Annalen der Physik und Chemie, **2,** p. 359; 1877.
(*j*) von Than, Annalen der Physik und Chemie, **13,** p. 84; 1881.
(*k*) Berthelot, Annales de chimie et de physique, **23,** p. 176; 1881.
(*l*) Berthelot and Matignon, Annales de chimie et de physique, **30,** 547; 1893.
(*m*) Mixter, Am. J. of Sci., **16,** p. 214; 1903.
(*n*) Rumelin, Zeitschrift für physikalische Chemie, **58,** p. 449; 1907.
The data obtained are reviewed in Section XII of this paper.

[2] The source of this uncertainty is explained in Section XII, p. 28 of this paper.

the calorimeter at some average temperature t_1. In a calibration experiment, the same temperature rise of Δt degrees, at the same average temperature t_1, was brought about in the same calorimeter by a measured quantity of electrical energy, E joules. In this manner, the formation of m grams of water was found to be equivalent, in energy involved, to E joules of electrical energy.

In this substitution method many of the systematic errors of the calorimetry itself are eliminated, since they tend, in general, to affect both kinds of experiments similarly, and systematic errors in the value found for the heat of formation of water are to be expected to originate principally in the determination of the mass of H_2O formed and of the quantity of electrical energy. Accurate standards of mass

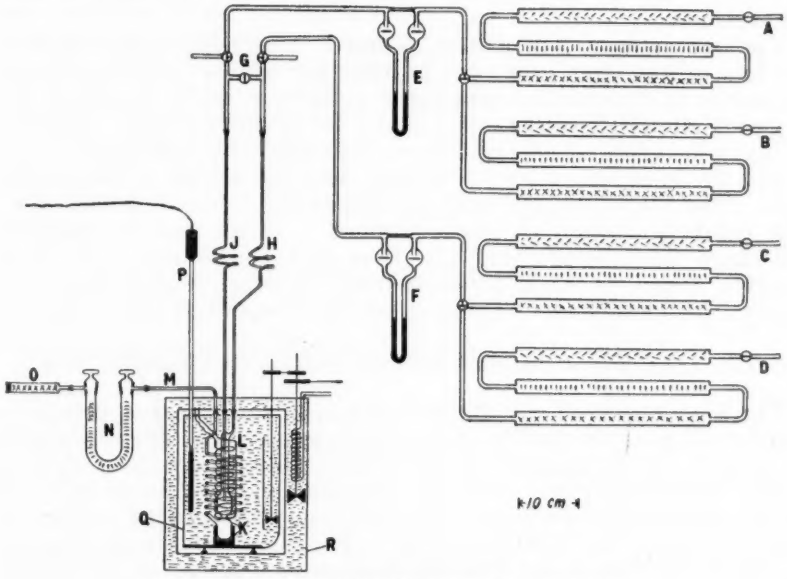

FIGURE 1.—*Schematic diagram of the apparatus*

A, B, C, D, purifying tubes; *E, F,* flow meters; *G,* stopcocks; *J, H,* inlet tubes; *K,* reaction vessel and support; *L,* calorimeter heater; *M,* connecting tube; *N,* U-tube absorber; *O,* guard tube; *P,* platinum thermometer; *Q,* calorimeter can; *R,* jacket.

and of the ohm, the volt, and the second were available at this bureau. High precision was obtained by the use of proper calorimetric technic, a platinum resistance thermometer with a sensitive galvanometric system for measuring changes of temperature, a sensitive potentiometric system for measuring the electrical power input, a precise timing device, and a suitable balance for determining the mass of H_2O formed.

III. APPARATUS ASSEMBLY

The assembly of the apparatus, exclusive of the measuring instruments, is shown to scale in Figure 1. All the parts through which the hydrogen and oxygen gases travel are made of Pyrex laboratory glass.

A, B, C, and *D* are each the entrance to a set of three purifying tubes which contain in order (1) "ascarite" (a sodium hydroxide-

asbestos mixture) for removing CO_2 and other acidic oxides, (2) "dehydrite" ($Mg(ClO_4)_2.3H_2O$) for removing water vapor, and (3) P_2O_5 for removing the last traces of water vapor. For the experiments in which hydrogen was burned in oxygen, *A* and *C* were attached, respectively, to the cylinders of pure compressed hydrogen and oxygen used in the combustion, and *D* was connected to an extra cylinder of oxygen. This second cylinder of oxygen was used to flush out the system and to vaporize the H_2O collected as liquid in the condensing chamber of the reaction vessel so that it would be absorbed in the weighed tube *N*. For the experiments in which oxygen was burned in hydrogen, the connections to *A* and *C* were reversed, and to *D* was connected an extra cylinder of hydrogen replacing the extra cylinder of oxygen already mentioned. The train *B* was not used in these experiments.

The two mercury flow meters, *E* and *F*, were calibrated to indicate the flow of hydrogen or oxygen in liters per minute. The two 3-way stopcocks at *G* permitted wasting of either gas, while the connecting stopcock allowed flushing of both inlet tubes with one gas. The coils on the inlet tubes, *J* and *H*, served to permit easy assembly.

L is the heating coil used to impart electrical energy to the calorimeter. The reaction vessel with its supporting frame is shown at *K*. The calorimeter can, *Q*, also contained a stirrer and the platinum resistance thermometer *P*. The tube *M* joins the exit tube of the reaction vessel to the U-tube absorber *N*, which was charged with "dehydrite" and P_2O_5. The guard tube *O* was filled with P_2O_5.

IV. THE REACTION VESSEL AND ITS OPERATION

The reaction vessel, shown in Figure 2, was designed to permit the reaction to proceed quietly at constant pressure with one of the gases burning in an atmosphere of the other. This vessel was made of Pyrex laboratory glass with the exception of the burner tube, the tip of which was silica glass. The silica-to-pyrex graded seal on this tube is about 5 cm from the tip *F*. The glass vessel was supported by the brass frame *J*. The platinum wire leads at *A* were sealed through the two inlet tubes, *B* and *C*, and continued down into the inlet tubes of the reaction vessel where the continuity was broken by a gap of about 2 mm. Two other pieces of platinum wire, coiled at the top to assure rigidity in the tubes, extended down into the reaction chamber, one outside and one inside the burner tube.

The spark which ignited the gas issuing from the burner tube jumped across the gap at the tip *F*. The flame, some 5 mm long, burned quietly at *F* in the reaction chamber *G*. The H_2O formed as a vapor in *G* condensed and collected as a liquid in the condensing chamber below. The excess gas, plus a small amount of H_2O vapor, passed from the condensing chamber at *H*, through the cooling coil *E*, and out through the exit *D*.

In an actual combustion experiment the entire reaction vessel was first flushed out and filled with the excess gas, which in some experiments was oxygen and in others hydrogen. When, for example, the entire reaction vessel had been filled with hydrogen flowing at the desired rate, and the rate of flow of the oxygen, flowing through its waste tube (*G*, fig. 1) had been adjusted properly, the oxygen was switched into the tube *B*. One or two seconds later the spark-coil

switch was closed, and the spark was permitted to jump across the gap at *F* for a measured number of seconds, two to six. This ignited the oxygen and the flame burned quietly in an atmosphere of hydrogen. The amount of hydrogen gas and water vapor issuing from the condensing chamber at *H* could be made to approach zero by reducing the amount of hydrogen gas to the stoichiometrical quantity required for its reaction with oxygen.

The platinum wires which formed part of the spark-coil circuit were made discontinuous at their entrance into the reaction vessel in order that the heat flow between the calorimeter system and its surroundings would be the same in the combustion experiments as in the calibration experiments with electrical heating where the reaction chamber remained cold.

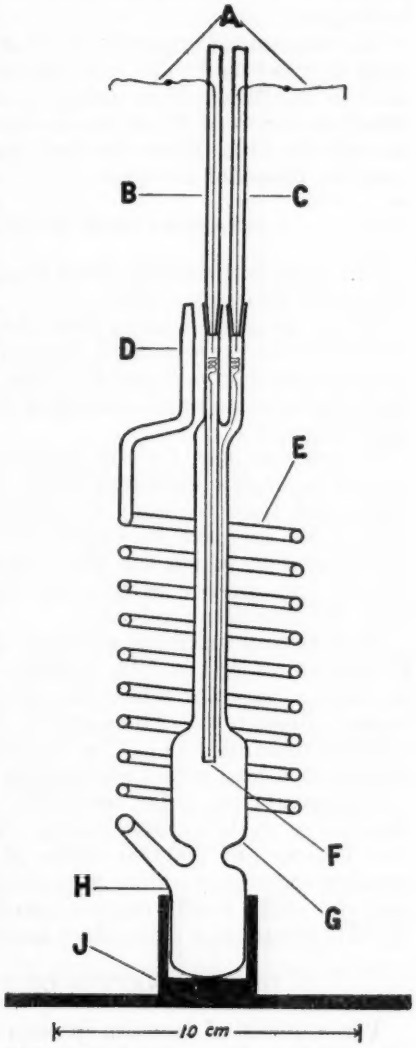

FIGURE 2.—*Cross section of the reaction vessel and supporting frame*

A, leads of spark circuit; *B*, *C*, inlet tubes; *D*, exit tube; *E*, cooling coil; *F*, burner tube; *G*, reaction chamber; *H*, condensing chamber; *J*, supporting frame.

V. THE CHEMICAL PROCEDURE

1. THE HYDROGEN AND OXYGEN

The amount of reaction in each combustion experiment was determined from the mass of H_2O formed, not from the mass of the H_2 or the O_2 consumed. It was, therefore, necessary only to obtain supplies of hydrogen and oxygen which contained no reactive gases other than O_2 or H_2. The presence of inert and nonreactive gases would not influence the experiments, either chemically or calorimetrically. This being the case, an examination of the reaction products would give definite and complete evidence as to the purity of the reaction.

Both the hydrogen and oxygen were regular commercial products obtained in steel cylinders. The former was of electrolytic and the latter of atmospheric origin. Analysis of the hydrogen and of the oxygen, after the gases had been passed through the purifying train shown in Figure 1, was made by the gas chemistry section of this bureau, in an improved gas analysis apparatus described in another paper.[3]

[3] G. M. Shepherd, B. S. Jour. Research, **6** (RP266), p. 121; 1931.

The amount of inert gas in the oxygen was found, in two analyses, to be 0.63 and 0.52 per cent. This inert gas was about two-thirds nitrogen and one-third argon plus neon. The presence of the rare gases in the oxygen offered no difficulty, but the N_2 might lead to the formation of a small amount of NH_3 when oxygen was burned in hydrogen.

The amount of impurity in the hydrogen which was noncombustible with O_2 was found to be 0.06 per cent in one determination and 0.09 per cent in another. This impurity was probably O_2. The presence of small amounts of O_2 in the hydrogen (or of H_2 in the oxygen) was unobjectionable, since the two gases were brought together in the reaction chamber anyway.

2. EXAMINATION OF THE REACTION PRODUCTS

The reaction products were examined for the presence of CO_2, SO_2, NH_3, and nitrogen oxides.

When the gases issuing from the reaction chamber during and after a combustion were passed through a saturated solution of $Ba(OH)_2$, no precipitate was formed. This test excluded the presence of CO_2 from the reaction products and of any carbon compound in the oxygen and hydrogen.

In order to test for the presence of SO_2, the exit gases were first passed through a glass-stoppered U-tube containing "dehydrite" and P_2O_5, and then through a weighed tube containing "ascarite" and P_2O_5. No increase in weight of the second tube was found in an experiment in which the first tube absorbed 6 g of H_2O. This test proved the absence of SO_2, as well as CO_2 and other acidic oxides, from the reaction products.

Acid ferrous sulphate solution, of the composition[4] best suited for absorption of NO or NO_2 to form the dark brown $Fe(NO)^{++}$, showed no change in color when the gaseous products of combustion were passed through it. The solution as used would have detected about 0.00003 mole of NO. The formation of this amount of NO would introduce a heat effect amounting to about 1 part in 20,000.

A quantitative color test with Nessler's reagent showed that the amount of NH_3 formed during the burning of oxygen in hydrogen was 1 mole per 250,000 moles of H_2O. This test was repeated in another experiment after vaporizing all the H_2O from the condenser, and the same result was obtained. The formation of this amount of NH_3 produces a heat effect amounting to about 1 part in 300,000.

3. DETERMINATION OF THE MASS OF H_2O FORMED

The amount of reaction in each combustion experiment was determined from the mass of H_2O formed. In each experiment, $m_{(H_2O)}$, the mass of H_2O formed, was equal to $m_1+m_2+m_3$. Here m_1 was the H_2O remaining as liquid in the condensing chamber, m_2 was the H_2O in the vapor phase within the reaction vessel, and m_3 was the H_2O carried as a vapor by the excess gas into the absorber (N, fig. 1) during the combustion period.

[4] Mellor, Treatise on Inorganic and Theoretical Chemistry, 8, p. 424, Longmans, Green & Co., New York; 1928.

The average amount of H_2O formed in a combustion experiment was about 2.85 g, practically all liquid. m_3 was equal to the increase in weight of the absorber during the time of the combustion. At the completion of the calorimetric observations dry gas (oxygen when hydrogen was burned in oxygen, and hydrogen when oxygen was burned in hydrogen), at a rate of about 0.5 liter per minute, was passed through the reaction vessel. It was found by experiment that even with rates of flow up to 0.9 liter per minute, and with the gas completely saturated with water vapor, the U-tube absorbed all the H_2O within ± 0.1 mg. In about 6 to 12 hours, all the H_2O which had been in the reaction vessel, either as a liquid or as a vapor, was carried out into the absorber N. This second increase in weight gave m_1+m_2. The amount of H_2O not condensed to liquid during a combustion was m_2+m_3. The magnitude of m_3 depended on the amount of excess gas and could be made to approach zero by reducing the proportion of the excess gas to the stoichiometrical amount. The magnitudes of the three masses were usually as follows: m_1, 2.85 g; m_2, 0.0012 g (at 26.5° C.) or 0.0016 g (at 31.5° C.); and m_3, 0.007 to 0.020 g. m_3 was in one case purposely made as large as 0.077 g.

The U-tube absorber (N, fig. 1) was made of soft glass with ground glass stoppers and ground ends. When in use, the U-tube stoppers and all the other joints in the gas train were lubricated with a "general" lubricant [5] made in the gas chemistry section of this bureau. The U-tube (N, fig. 1) was 16 cm long and 6 cm wide, with a cross section of about 1.8 cm^2 and an internal volume of about 60 cm^3. For use in the absorption of H_2O, this tube was freshly filled with "dehydrite" and with a 2 cm layer of P_2O_5 at the exit end. Layers of clean, dry, acid-washed asbestos bounded the "dehydrite" and the P_2O_5.

The apparent increase in mass of the absorber after it had received all the H_2O formed in a given experiment was corrected to vacuum in order to obtain the true mass of the H_2O. This correction to vacuum required a knowledge of the increase in volume of the "dehydrite" upon the absorption of a given amount of H_2O. When $Mg(ClO_4)_2.3H_2O$ absorbs H_2O to form $Mg(ClO_4)_2.6H_2O$, the increase in volume is 0.60 cm^3 per gram of H_2O absorbed. This was calculated from the following densities, in grams per cm^3: $Mg(ClO_4)_2.3H_2O$, 2.044; $Mg(ClO_4)_2.6H_2O$, 1.970.[6]

The correction to vacuum was made as follows: After the absorber was properly charged with "dehydrite" and P_2O_5, lubricated, and thoroughly flushed out with the gas which was to be in excess in the combustion experiment to follow, the U-tube and its counterbalance were placed in the balance case. With one U-tube as the absorber and a second U-tube, equal in external volume, for a counterbalance, changes in the density of the air in the balance case would affect only the buoyancy on the brass weights. The counterpoise was closed and contained a fixed mass of air in all the weighings.

In order to produce equilibrium of the beams of the balance, m grams of brass weights were added to the right pan. Omitting the masses of the U-tubes, whose air buoyancies cancel, the initial balance was:

$$m_{(s)}+m_{(g)}=m-m_{(air)} \qquad (1)$$

[5] Shepherd and Ledig, Ind. Eng. Chem., **19**, p. 1059; 1927.
[6] International Critical Tables, **1**, p. 141.

where $m_{(s)}$ was the mass of the solid matter in the absorber, $m_{(g)}$ was the mass of the gas in the absorber, m was the mass of the brass weights, and $m_{(air)}$ the mass of the air displaced by the brass weights.

After all the H_2O formed was taken up in the U-tube absorber, a new balance was made:

$$m'_{(s)} + m'_{(g)} = m' - m'_{(air)} \tag{2}$$

Here $m'_{(s)}$ was the mass of the solid matter now in the absorber. Since the volume of the solid in the absorber had increased, there was a numerically equal decrease in the volume of the gas in the absorber. The mass of the gas was now $m'_{(g)}$ while m' was the new mass of the brass weights, and $m'_{(air)}$ was the mass of the air displaced by these brass weights. $m'_{(s)}$ was equal to $m_{(s)}$ plus $m_{(H_2O)}$, the true mass of the H_2O absorbed. One may then write

$$m_{(s)} + m_{(H_2O)} + m'_{(g)} = m' - m'_{(air)} \tag{3}$$

Subtracting equation (1) from (3),

$$m_{(H_2O)} = (m' - m) + (m_{(g)} - m'_{(g)}) - (m'_{(air)} - m_{(air)}) \tag{4}$$

$m' - m$, or Δm, was the apparent increase in mass of the absorber and was less than $m_{(H_2O)}$ by about 7 parts in 10,000 with oxygen in the absorber and was greater than $m_{(H_2O)}$ by about 1 part in 10,000 with hydrogen in the absorber. $m_{(g)} - m'_{(g)}$ was the mass of that volume of gas in the absorber which had been displaced by the increase in volume of the solid. $m'_{(air)} - m_{(air)}$ was the mass of that volume of air occupied by the brass weights of mass, Δm. With the density of the air in the balance case equal to 0.0012 g per cm^3, and that of the brass weights equal to 8.4 g per cm^3, $m'_{(air)} - m_{(air)}$ was equal to 0.00014 g for $\Delta m = 1$. With oxygen in the U-tube absorber at 25° C. and 1 atmosphere, and for $\Delta m = 1$,

$$m_{(g)} - m'_{(g)} = 0.60 \times 0.00131 = 0.00079 \text{ g} \tag{5}$$

With hydrogen in the absorber

$$m_{(g)} - m'_{(g)} = 0.60 \times 0.000082 = 0.00005 \text{ g} \tag{6}$$

For the experiments in which oxygen was the excess gas

$$m_{(H_2O)} = (1 + 0.00079 - 0.00014) \times \Delta m = 1.00065 \Delta m \tag{7}$$

With hydrogen as the excess gas

$$m_{(H_2O)} = (1 + 0.00005 - 0.00014) \times \Delta m = 0.99991 \Delta m \tag{8}$$

In order to check this method of determining the true mass of H_2O, extra weighings were made in some experiments with each gas in the absorber both before and after the absorption. In this manner, $m_{(H_2O)}$ with oxygen in the absorber agreed with the value of $m_{(H_2O)}$ with hydrogen within 1 to 7 parts per 100,000. The accuracy of the correction to vacuum, while ample in both cases, is much more

certain with hydrogen in the absorber because its density is only one-sixteenth that of oxygen.

In the actual experiments in which oxygen filled the absorber, the change in the density of the oxygen in the absorber between weighings was corrected for by calculation from the changes in its temperature and pressure. The mass of oxygen in the charged absorber was approximately equal to 16/15 times the decrease in weight of the absorber when the oxygen was replaced with hydrogen. Since the mass of the oxygen was usually 0.065 g, the total correction due to the change in the density of the oxygen in the absorber was -0.00022 g per degree increase in temperature at about 25° C. and 0.000086 g/mm increase in pressure at a pressure of about 1 atmosphere. The corresponding corrections for hydrogen were one-sixteenth of these values. This correction is independent of the amount of H_2O absorbed.

Many blank experiments were made by passing oxygen or hydrogen through the entire system connected as shown in Figure 1. The observed changes in mass of the absorber in these blank experiments were always zero within 0.1 to 0.2 mg. In order to obtain blanks of this order, great care was needed in the manipulation and handling of the U-tube and none but properly lubricated ground-glass joints were used throughout the gas train. Only the stoppers of the U-tube were touched by hand, while the U-tube proper was handled in clean bleached cheesecloth. The lubricant on the connecting joints of the U-tube was carefully removed with ether before each weighing. In weighing, uniformity of procedure was employed in order that unknown constant errors, if any existed, would cancel. The balance employed was located in the same room close to the calorimeter and was, therefore, at all times subjected to the same constant atmospheric conditions as was the absorption tube. For this reason and the fact that the absorber was not touched by hand, the time for establishment of equilibrium in the balance case was about 20 minutes. Accordingly, all weighings were made 20 minutes after the absorber was placed in the balance case. The entire system, as well as the absorber, was thoroughly flushed out before each experiment.

The weights used were calibrated against the mass standards of this bureau by the mass section. The ratio of the arms of the balance used in these weighings was $\frac{L}{R}=1.000007$. The weighings were made to the nearest 0.05 mg.

VI. CALORIMETRIC APPARATUS AND MEASURING INSTRUMENTS

1. THE CALORIMETER AND THE THERMOMETRIC SYSTEM

A schematic cross section of the calorimeter, which with some minor changes was the one used in this laboratory [7] to determine the heat of formation of SO_2, is given in Figure 1. R is the constant-temperature water jacket with its heater and stirrer. A 20-junction thermel (thermoelement) used for reading the variations in the temperature of the jacket water, is not shown. Q is the calorimeter can containing its stirrer, K is the reaction vessel and supporting frame, P, the platinum resistance thermometer, and L, the heating

[7] Eckman and Rossini, B. S. Jour. Research, 3, p. 597; 1929.

coil. The air space between the calorimeter can and the jacket was about 1 cm. The calorimeter can was supported on three ivory cones and contained about 3,700 g of distilled water.

The platinum thermometer was immersed to the same marked depth in all the calorimetric experiments. A counted number of drops of oil, usually six, was placed on the surface of the water in the calorimeter can at the openings in order to reduce evaporation. The three openings in the cover of the calorimeter can, which coincided with holes in the jacket cover, served to permit the passage of (1) the platinum resistance thermometer P, (2) the connecting tubes, J, H, and M, to the reaction vessel, and (3) the leads to the heating coil.

A special room, of dimensions 10 by 10 by 30 feet, was used to house all the apparatus. With the window, door, and ventilating openings closed, the temperature of this room changed not more than 0.1° or 0.2° C. per hour, and it was thus possible to maintain the temperature of the jacket water constant simply by passing a steady current through the jacket heater. This current was regulated manually as need required.

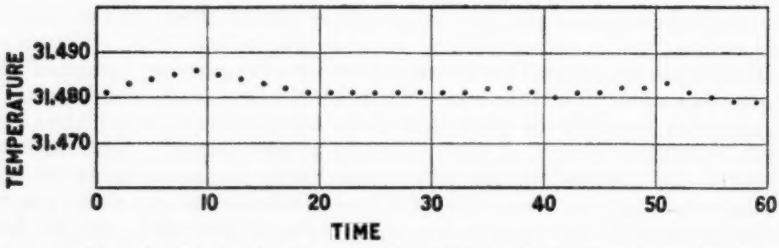

FIGURE 3.—*A plot showing the variation of the jacket temperature with time*

The ordinate scale gives the temperature in °C. while the abscissa scale marks the time in minutes. The data are from experiment S–AA.

In Figure 3, the jacket temperature (data from combustion experiment S–AA) is plotted against the time. The jacket temperature was read every two minutes by means of the 20-junction copper-constantan thermel and, at the conclusion of each experiment the thermel was compared directly with the platinum resistance thermometer. The data illustrated in Figure 3 show that the temperature of the jacket changed very little in the course of a run and these changes were known at each instant to 0.001° C.

In all of the calorimetric experiments, the temperature of the calorimeter can and contents was below that of the jacket, and the rate of heat transfer from the latter to the former was such as to increase the temperature of the calorimeter can and contents about 0.002° C. per minute per °C. difference in temperature.

The speed of stirring of the calorimeter water, which varied not more than 1 or 2 per cent over the time of each experiment, ranged from 200 to 240 r. p. m. The energy contributed by this stirring was about 4 joules per minute for a speed of 200 r. p. m.

The platinum resistance thermometer and bridge had been used in a previous investigation in this laboratory.[8] The constants of the

[8] See footnote 7, p. 9.

thermometer then were: $R_0 = 25.6230$ international ohms; $R_{100} - R_0 = 10.0136$ international ohms; $\delta = 1.487$. R_0 was again measured by the thermometry section of this bureau, and found to be 25.6233 international ohms.

The transfer values used for $\frac{dR}{dt}$ and $\frac{d^2R}{dt^2}$ are:

	25° C.	30° C.	
$\frac{dR}{dt}$	0. 100880	0. 100731	ohm/° C.
$\frac{d^2R}{dt^2}$	−. 000030	−. 000030	ohm/° C./° C.

The method of converting an increase in resistance of the platinum thermometer into a temperature rise in degrees is described in previous papers,[9] [10] but such conversion is, of course, not necessary and is made for psychological purposes only.

The resistance of the platinum thermometer was read on a Mueller thermometer bridge (Leeds & Northrup No. 47669). A high powered telescope, placed about 1 m from the galvanometer, was focused on the galvanometer mirror which reflected a highly illuminated scale placed in a box mounted on the wall opposite the galvanometer, some 8 m distant. The sensitivity of the galvanometer was such that a change of 0.0001 ohm was equivalent to a change of 5.2 mm on the galvanometer scale, so that, approximately, 1 mm was equivalent to 0.0002° C. Readings on the galvanometer scale could be estimated to 0.1 mm.

The coils of the thermometer bridge were not kept in a thermostat. This fact did not militate greatly against the precision obtained in the calorimetric experiments because (1) the temperature of the room was not more than 2° to 3° C. different in the various calibration and combustion experiments of a given set and (2) the variation of the room temperature during an experiment was but 0.1° or 0.2° C. per hour. The temperature coefficient of resistance of the 0.1 ohm coils of the measuring bridge was about 10 parts per million per degree increase in room temperature. In two experiments made at constant room temperatures which differed by 1° C., the error on conversion of the increase in thermometer resistance into ° C. would be 1 part in 100,000. The possibility of error arising from the second factor listed above is much greater, but this source of error was eliminated by the manner of recording the data. The gradual change in the room temperature would change the reading of the thermometer even though its resistance were constant, but as 20-minute observation periods were made before and after the 20-minute reaction period, the gradual changes in resistance of the coils in the thermometer bridge due to the gradual and uniform change in room temperature became incorporated as part of the drift in the "fore" and "after" periods. The completeness of the elimination of this error depends upon the constancy of the rate of change of the room temperature during the time of the observations.

The resistance coils in the thermometer bridge were calibrated by the resistance measurements section of this bureau.

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[9] Dickinson and Mueller, B. S. Bull. **9**, p. 483; 1913.
[10] See footnote 7, p. 9.

The temperature of the jacket was determined with a 20-junction copper-constantan thermel, with one leg at 0° C. in a vacuum flask containing ice and water and the other in the well-stirred jacket water. The e. m. f. of the thermel was read every two minutes on a White double potentiometer (Leeds & Northrup No. 156585). The thermel was calibrated against the platinum thermometer so that small changes of e. m. f. could be converted into ohms. This factor was 80 micro volts per 0.01 ohm. At the conclusion of each experiment the platinum thermometer was placed in the water jacket, and the thermel was compared directly with it.

2. THE ELECTRICAL ENERGY SYSTEM

The heating coil, shown as *L* in Figure 1, was made by drawing down thin copper tubing over double silk covered No. 36 B. and S. gage constantan wire which had previously been covered with a thin coating of bakelite. The resistance wire was insulated throughout from the copper tube inclosing it. The leads to the resistance coil were No. 24 B. and S. gage enameled copper wire. A 1-inch piece of thin ⅛-inch copper tubing, insulated from the wire, was placed over the region where the copper leads were soldered to the resistance wire. In this manner the circuit for the heating current was completely insulated from the calorimeter water and can.

The copper leads were brought up through an opening at the edge of the cover of the calorimeter can, and after crossing the 1 cm air space were cemented firmly with de Khotinsky wax to the calorimeter jacket. No. 28 B. and S. gage copper leads, for measuring the voltage drop across the heating coil, were soldered to the current leads midway between their point of contact with the calorimeter water and the jacket. All the leads were in good thermal contact with, but electrically insulated from, the calorimeter water and the jacket. Actually, the point at which the potential leads were attached to the current leads was slightly closer to the jacket than to the calorimeter water. The potential readings were corrected for this small difference, a displacement of 1 mm being equivalent to about 2 parts per 1,000,000 of the reading.

The electrical energy input into the calorimeter was determined by measuring (1) the potential drop across the heating coil and (2) the potential drop across a standard resistance through which passed the same current (less a small calculable amount which flowed through the potential coils in parallel with the heating coil). These voltages were measured on a White double potentiometer having a range of 100,000 microvolts. The sensitivity of these measurements was such that 1 mm on the galvanometer scale (1 m distant from the galvanometer) was approximately equivalent to 2 microvolts. The scale readings were estimated to 0.1 mm.

The energy-measurement circuit is shown in Figure 4. At *A* are the leads from a storage battery of 70 volts. *B* designates the external stabilizing resistance, equal to the resistance of the calorimeter heater. *C* represents the calorimeter heater. The potential drop across the standard 0.1 ohm resistance at *D* was measured on the potentiometer at *H*. *E* and *F* are standard resistances of 10,000 and 10 ohms, respectively. The potential drop across *F* was measured on the potentiometer at *G*.

In this manner the current through the calorimeter heating coil C is given by $\frac{1}{r_D}\left(1-\frac{r_C}{r_E+r_F}\right)e_H$, the potential measured at H. The potential drop across the heating coil C is equal to $\frac{r_E+r_F}{r_F}e_G$, the voltage measured at G. The readings of e_H, which serve as a measure, of the current through the calorimeter, are shown in the upper part of Figure 5; while the readings of e_G, which measure the voltage drop across the heating coil, are plotted in the lower part. These data are the actual readings taken in experiment S–2. Readings of e_H and e_G were made, respectively, on the P and Q dials of the potentiometer within 10 or 15 seconds of each other on the half minute. The operator then was free to take the platinum theremometer readings on the even minute.

As can be seen from the data plotted in Figure 5, the variation of the current and voltage is small enough so that the energy input can be calculated as the product of the time, the average current, and the average voltage. The difference between this simple method of deter-

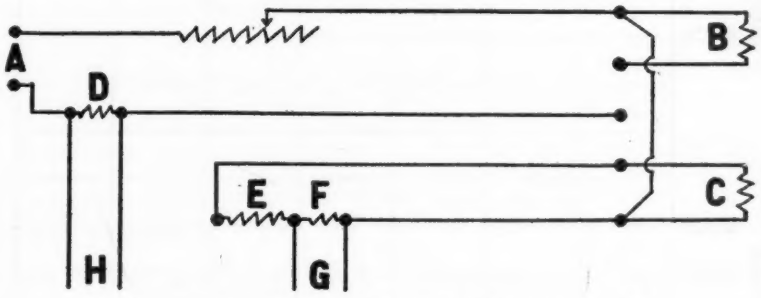

FIGURE 4.—*Diagram of the electrical energy circuit*

A, 70-volt storage battery; *B*, external stabilizing resistance; *C*, calorimeter heater; *D*, *E*, *F*, standard resistances of 0.1, 10,000, and 10 ohms, respectively; *G*, *H*, leads to potentiometer.

mining the energy input, and the more exact but laborious method of integrating the watts input, is not greater than 1 or 2 parts per 1,000,000, for any of the energy data taken.

The standard cell used with the potentiometer to measure E_H and E_G was compared, both before and after the experiments were performed, with the standard cells of this bureau, while the resistances D, E, and F, and the resistance coils of the potentiometer, were similarly compared with those of this bureau. The accuracy of these standardizations was certified to 1 part in 20,000 for r_D and r_F, to 1 in 10,000 for r_E, to 1 in 50,000 for the standard cell, and to 1 in 10,000 for the potentiometer readings (when over 20,000 microvolts).

The time of the electrical energy input was 11 to 13 minutes. In the first set of experiments this time interval was measured on a Gaertner chronograph having two pens recording on a revolving cylinder. The seconds impulses were transmitted to the chronograph from the master clock in the time section of this bureau. One of the two pens marked each second while the other pen was in circuit with one side of a special V-type quick acting double-pole double-throw knife switch whose other side was part of the electrical energy circuit.

The throwing of this switch simultaneously sent energy into the calorimeter and recorded the time on the chronograph paper. The alignment of the two knife-edges of the switch with their respective clip receptacles was checked, and in several blank time experiments, the two sides of the switch recorded the same time within 0.02 second. The cylinder was 15 cm in diameter and revolved at such a rate that a point on its periphery moved about 16 mm per second. It is estimated that the accuracy of this device in measuring a time interval of 12 minutes is about 1 part in 20,000.

For the second set of experiments a new timing device was obtained. This timing device is the same as that of Johnston,[11] with some im-

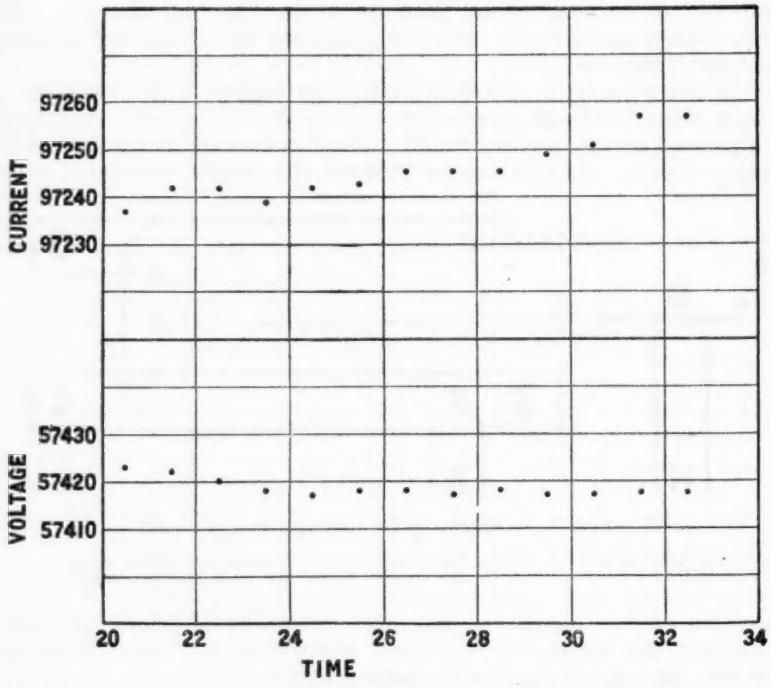

FIGURE 5.—*Plot showing the variation of the current readings and of the voltage readings with time*

The ordinate scale measures the actual potentiometer readings in microvolts, while the abscissa scale gives the time in minutes.

provements suggested by him. The principal improvement consists of a device for preventing the main sprocket wheel (marked *W* in the descriptive sketch)[11] from rotating more than one notch per impulse. This is accomplished by having two sprocket wheels, firmly joined to each other, one of which receives the impulses from the shaft *B* while the other is equipped with a back stop to prevent rotation of more than one notch.[12]

Measured with this timing device, the time of the electrical energy input (about 700 seconds) is estimated to be accurate to 1 part in 100,000.

[11] Johnston, J. Opt. Soc. Am. and Rev. Sci. Inst., **17**, p. 381; 1928.
[12] This timing device was built by G. F. Nelson, Berkeley, Calif.

VII. MOLECULAR WEIGHTS, CONSTANTS, UNITS, FACTORS

The atomic weights of oxygen and hydrogen were taken as 16.000 and 1.0078, respectively. [13]

The unit of electrical energy used in this investigation is the international joule and is that defined by (1) the international ohm as maintained at this bureau by standard resistance coils, (2) the international volt as maintained at this bureau by standard cells, and (3) the mean solar second.[14]

The factor 1.0004 is used to convert international into absolute joules.[15]

In order to correct the slightly varying amounts of water in the calorimeter can to a common mass, the heat capacity of water was taken as 4.175 and 4.173 international joules per gram at 25° and 30° C., respectively. To correct the heat capacity of the water to a common average temperature, the temperature coefficient was taken as −0.00050 and −0.00027 joule per gram per degree per degree at 25° and 30° C., respectively.[16]

For the reaction

$$H_{2(gas)} + \tfrac{1}{2}O_{2(gas)} = H_2O_{(liquid)} \qquad (9)$$

ΔC_p at 25° C. is calculated to be 32 joules per mole [16]; that is, Q, the heat evolved in the reaction, decreases 32 joules per degree increase in temperature. This value was used in correcting values of the heat of formation to a common temperature.

In calculating the "vaporization" energy corrections to the heat of reaction, the heat of vaporization of water was taken as 2,439 and 2,428 joules per gram at 25° and 30° C., respectively.[17]

For the purpose of converting the data of other investigators, 1 g-cal.$_{15}$ is taken equal to 4.185 absolute joules, or $\frac{4.185}{1.0004}$ international joules, and the heat capacity of water at various temperatures is calculated from the Callendar formula: [18]

$$c = 0.98410 + \frac{0.504}{t+20} + 0.0084\ \frac{t}{100} + 0.009\left(\frac{t}{100}\right)^2 \qquad (10)$$

In this formula, t is in °C., and c gives the heat capacity in g-cal.$_{15}$

[13] Baxter, 1930 Report of the Committee on Atomic Weights, J. Am. Chem. Soc., **52**, p. 861; 1930.

[14] Standards of the international ohm and the international volt are similarly maintained in the other national laboratories of the world. On the basis of intercomparisons reported during the last five years, the international joule derived from the standards so maintained by the various countries differs from that in the United States by the amounts shown in the following table:

Country	Difference
	Per cent
Germany	−0.013
Great Britain	+.001
France	−.009 (?)
Japan	+.003
United Socialist Soviet Republics	−.012

This information is furnished by the electrical division of this bureau.

[15] This conversion factor is that recommended in the Technical New Bulletin of the Bureau of Standards, No. 156; April, 1930.

[16] International Critical Tables, **5**, pp. 78, 80, and 82.

[17] Osborne, Stimson and Flock, B. S. Jour. Research, **5**, p. 479; 1930

[18] Callendar, Trans. Royal Soc. London (A) **212**, p. 1; 1912.

VIII. THE PRELIMINARY AND CORRECTION EXPERIMENTS

1. CALORIMETRIC PROCEDURE

In all the calorimetric experiments at 25° C., the jacket temperature was maintained constant at 26.5° C., and the initial and final temperatures of the calorimeter water were, respectively, 23.5° and 26.5° C. For the experiments at 30° C., the corresponding temperatures were 31.5° C. for the jacket and 28.5° and 31.5° C. for the calorimeter water.

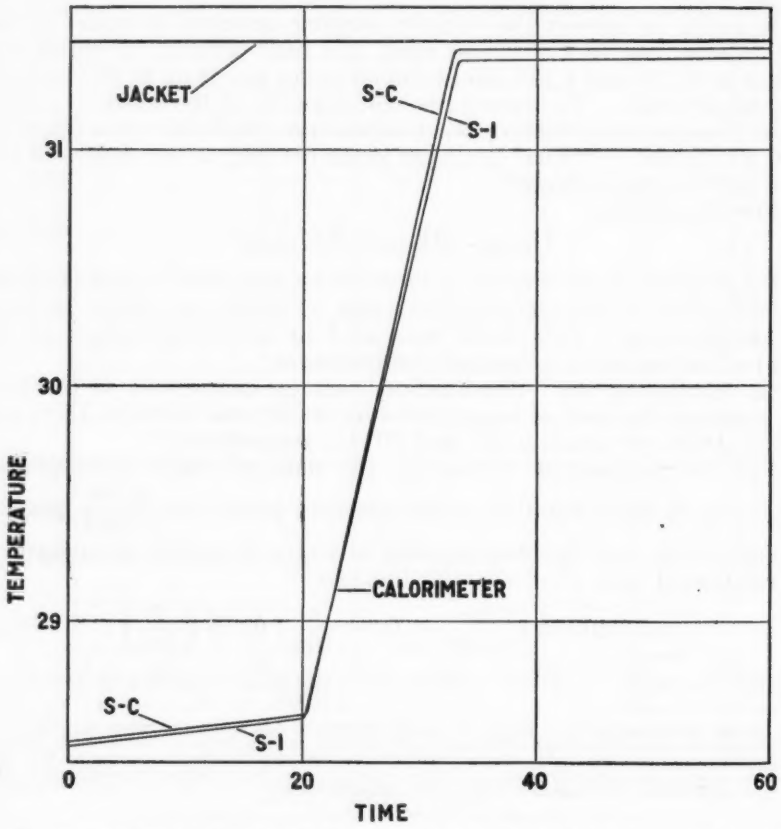

FIGURE 6.—*Plot showing the variation of the calorimeter temperature with time*

The ordinate scale gives the temperature in °C. and the abscissa scale marks the time in minutes. Curve *S-I* is for electrical calibration experiment *S-I*, and curve *S-C* is for combustion experiment S-C.

In each experiment the observations were divided into three periods. First, the "fore" period of 20 minutes in which readings of the calorimeter water and the jacket temperatures were made. Second, the "reaction" period of 20 minutes in which electrical energy or combustion energy was supplied to the calorimeter water at a rate which brought it to the final temperature in 12 or 13 minutes, leaving a time of 7 or 8 minutes for attainment of equilibrium in the calorime-

ter system. In this period observations of the calorimeter water temperature were made every minute and of the jacket temperature every two minutes. For the calibration experiments readings of the current and voltage were made every minute. Third, the "after" period of 20 minutes in which readings of the temperature of the calorimeter water and of the jacket water were taken.

In Figure 6 are curves of the temperature of the calorimeter and of the jacket plotted against the time in minute. Curve *S*–1 represents the data of calibration experiment *S*–1 with electric heating, while curve *S*–*C* shows the data of combustion experiment *S*–*C*. These curves portray the substantial identity of the calorimetric conditions in the two kinds of experiments. With such a procedure, any unknown constant error in determining the true temperature rise is eliminated and does not affect the comparison of electrical with combustion energy.

The method of determining the true or corrected temperature rise, Δt, is explained in a previous paper.[19] In the text and the tables of the present paper, R represents the temperature reading of the calorimeter water expressed in ohms on the platinum thermometer; R_j is the jacket temperature reading converted into ohms on the platinum thermometer; Z is the time in minutes; a numerical subscript indicates the time in minutes at which the given observation was made; k is the proportionality factor, in ohms per minute per ohm, for the flow of heat energy from the jacket and surroundings to the calorimeter system; k measures, in ohms, the total amount of this temperature rise in the time from Z_{20} to Z_{40}, and is evaluated by multiplying k by the area, in Figure 6, which is bounded by the calorimeter and jacket lines and the ordinates at 20 and 40 minutes; u is the constant rate at which the calorimeter temperature increases (or decreases) and is chiefly due to the energy input of stirring and energy removal by evaporation; U measures, in ohms, the total amount of this temperature change in the time from Z_{20} to Z_{40}, and is equal to $(Z_{40}-Z_{20})\,u$ or $20\,u$.

From the observations taken in the "fore" period, one can write

$$u+\left(R_{j(0,\,20)}-\frac{R_0+R_{20}}{2}\right)k=\frac{R_{20}-R_0}{20} \tag{11}$$

The data of the "after" period give

$$u+\left(R_{j(40,\,60)}-\frac{R_{40}+R_{60}}{2}\right)k=\frac{R_{60}-R_{40}}{20} \tag{12}$$

These equations are solved for u and k in each experiment, whence U and K can be calculated as already indicated.

The main temperature rise of the calorimeter system is measured by

$$R_{40}-R_{20}=\Delta R \tag{13}$$

Then the corrected temperature rise is equivalent to

$$\Delta R-U-K=\Delta R_{\text{corr}} \tag{14}$$

and the true or corrected temperature rise in degrees is obtained by

[19] See footnote 7, p. 9.

dividing ΔR_{corr} by the value of $\frac{dR}{dt}$ for the average temperature of the experiment.

$$\Delta t_{corr} = \frac{\Delta R_{corr}}{\frac{dR}{dt}} \tag{15}$$

The actual operations in a calibration experiment at 30° C. were:

(*a*) The current from the storage battery was switched to the external stabilizing resistance which had previously been made equal in resistance to the calorimeter heater.

(*b*) The temperature of the water in the calorimeter jacket was brought to 31.5° C. The current through the jacket heater was adjusted from time to time so that the jacket temperature remained constant.

(*c*) The clean, dry calorimeter can, with the supporting frame for the reaction vessel, was placed in position on the three ivory cones.

(*d*) The clean, dry reaction vessel, with the exit tube properly lubricated, was placed in the supporting frame.

(*e*) About 3,700 g of distilled water, whose temperature was about 27° C., was weighed to 0.01 g and carefully poured into the calorimeter can. This operation included weighing a clean beaker (with greased lip to facilitate pouring) before and after the water was poured from it. (Losses from evaporation in this operation were assumed to be the same for all experiments since a uniform procedure was employed. The actual loss by evaporation was found to be not more than 0.15 g, and the variability of this was negligible.)

(*f*) The tightly fitting cover of the calorimeter can was placed in position with its three openings properly aligned. Two drops of oil were added through each of the openings. The jacket cover was rotated into position. The platinum thermometer, the exit tube, and the two inlet tubes, properly lubricated, were placed in position. The stirring, both of the jacket and the calorimeter water, was begun.

(*g*) The temperature of the calorimeter water was brought up to 28.5° C. by means of the heating coil in the calorimeter water.

(*h*) Readings of the room temperature were made every 10 minutes.

(*i*) When equilibrium was established in the calorimeter system, observations were begun. Readings of the platinum thermometer and of the jacket thermel were made every two minutes in the "fore" period.

(*j*) At the twentieth minute, the timing device having been set, the current was switched into the calorimeter system and readings of the current, the voltage, and the platinum thermometer were taken every minute, while the jacket thermel was read about every two minutes. At the thirty-third minute the timing device switched the current back to the external stabilizing resistance.

(*k*) The "after" period ran from the fortieth to the sixtieth minute, and here observations of the platinum thermometer and jacket thermel readings were made every two minutes.

(*l*) The platinum thermometer was transferred from the calorimeter to the jacket water where the jacket thermel and platinum thermometer readings were taken simultaneously. The thermel

reading, in microvolts, was thus converted directly into ohms on the resistance thermometer.

The operations in the combustion runs were the same except that operation (*a*) was omitted, (*j*) was changed, and several others were added, as follows:

(*aa*) The U-tube absorber was cleaned, properly charged, flushed out, and filled with hydrogen, weighed, and placed in position with its guard tube, after the calorimeter system was thoroughly flushed out and filled with hydrogen. The ends of the U tube were lubricated after the weighing.

(*bb*) The rates of flow of hydrogen and oxygen were adjusted. Here hydrogen was in excess.

(*j*) The hydrogen was turned on at the twentieth minute. The oxygen was then turned on, and about two seconds later the spark circuit was closed for a measured time of two to six seconds. The oxygen was now ignited and burning quietly. Readings of the calorimeter temperature were taken every minute and of the jacket temperature every two minutes. At the proper time, around the thirty-second minute, the oxygen and hydrogen were turned off to waste.

(*m*) The U-tube absorber, with its guard tube and exit tube, was removed and closely joined (with a rubber tube connection) to the hydrogen waste tube. The exit *D* (fig. 2) was stoppered. Thus the small amount of H_2O which condensed in the tube *M* (fig. 1), when the room temperature was below the jacket temperature, was carried into the U-tube absorber. The tube *M* was replaced and its exit end was stoppered. The lubricant was removed from the ends of the U tube, which was then weighed and replaced in the system. (Blank experiments on this operation were made to make sure that no H_2O was taken up from the rubber. Dry gas passing through the waste tube removed any moisture which may have condensed on the rubber tube when not used in this operation.)

(*n*) A flow of dry hydrogen, about 0.5 liter per minute, was now sent into the reaction vessel, through both inlet tubes. At the end of 6 to 12 hours, when all the H_2O in the reaction vessel had been vaporized and carried into the U-tube absorber, the U tube was removed, the ends were cleaned with ether, and the final weighing was made.

2. EVALUATION OF "SPARK," "GAS," "AND "VAPORIZATION" ENERGY

In the combustion experiments, there were three sources or sinks of energy, in addition to the heat of the given reaction, which were not present in the calibration experiments. These were (1) the energy given to the calorimeter by the spark which was used to start the combustion, (2) the energy taken up from the calorimeter by the oxygen and hydrogen entering the calorimeter at a temperature lower than the average temperature of the calorimeter, and (3) the energy of vaporization of the H_2O not condensed to liquid. The approximate magnitudes of these energy items were, respectively, 2, 2 to 8, and 5 to 25, parts per 10,000, of the total energy of the experiment.

The value of the "spark" energy was determined by passing the spark into the calorimeter when its temperature was slightly below

that of the jacket. The time of sparking was made about ten times that employed in the combustion experiments. The resulting small temperature rise in the calorimeter measured the amount of this sparking energy. Two experiments were made, with the following results:

		I	II
Time of sparking	seconds	30	30
Energy	joules	54	56
Spark energy	joules/second	1. 80	1. 86
Average	do	1. 83	

The "gas" energy, which was that energy taken up by the inflowing gases entering at a temperature below the average temperature of the calorimeter, was calculated from the known heat capacity of the gases and the difference between their temperature (taken as that of the room) and the average temperature of the calorimeter. For this purpose the heat capacities of hydrogen and oxygen were taken as 28.6 and 29.2 joules per mole,[20] respectively.

The "vaporization" energy was that required to vaporize (1) the H_2O carried out of the calorimeter as a vapor by the excess gases and (2) the H_2O remaining in the reaction vessel as a vapor. The mass of the H_2O in (1) was determined by weighing the absorber before and after the combustion, as already described, and that in (2) was calculated from the known vapor pressure of water at 26.5° C. (and 31.5° C.) and the internal volume of the reaction vessel and tubes.

The internal volume was 51½ cm^3. From this was subtracted about 3 cm^3 occupied by the liquid H_2O formed. The mass of H_2O vapor in the reaction vessel at 26.5° and 31.5° C. was then 0.0012 and 0.0016 g, respectively. The heat of vaporization of H_2O was taken as 2,439 and 2,428 international joules per gram at 25° and 30° C., respectively.[21]

In several experiments, the "gas" energy and the "vaporization" energy were purposely made large in order to test the validity of the foregoing assumptions. In order to check collectively the corrections for "spark," "gas," and "vaporization" energy the following experiment was performed:

The calorimeter was brought to within 0.3° C. of the jacket temperature, which was 31.5° C. The "fore" period observations were taken in the usual manner. At the beginning of the "reaction" period, the combustion was started in the usual manner, but was stopped after a period of about 15 seconds. This was repeated twice. These three small combustions resulted in a temperature rise of the calorimeter due to the algebraic sum of (1) the heat of formation of the small amount of H_2O formed, (2) the "spark" energy, (3) the "gas" energy, and (4) the "vaporization" energy.

[20] International Critical Tables, 5, pp. 80 and 82.

[21] See footnote 17, p. 15.

The following data were obtained in this experiment:

Electrical equivalent of calorimeter system	int. joules/°C	15712. 0
Corrected temperature rise	°C	. 18501
E: Total energy	int. joules	2896. 7
Spark time	seconds	15
E_2: "Spark" energy	joules	27. 5
Volume of inflowing gases	liters	1. 09
Temperature difference between room and colorimeter	°C	−7. 0
E_3: "Gas" energy	joules	−9. 0
Mass of H_2O carried out of colorimeter as vapor	g	. 0157
Mass of H_2O remaining in reaction vessel as vapor	do	. 0016
Total H_2O formed as vapor	do	. 0173
E_4: "Vaporization" energy	joules	−41. 9
Total amount of H_2O formed	g	. 18416
E_1: Heat of formation of the H_2O (285,580 int. joules/mole at 31° C.)	int. joules	2919. 2

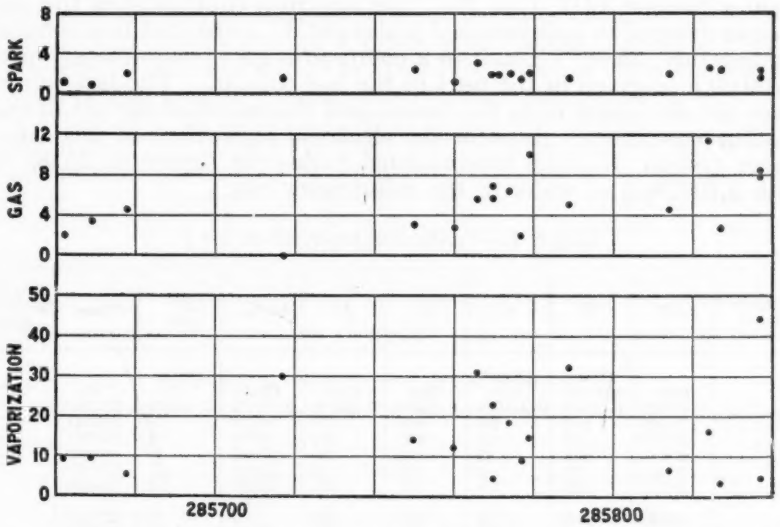

FIGURE 7.—*Plot showing the magnitude of the "vaporization," "gas," and "spark" energy relative to the total energy in each experiment, plotted against the heat of formation value obtained in that experiment*

The ordinates in each case are parts in 10,000 of the total energy while the abscissa give the values for the heat of formation in international joules per mole at 25° C. and 1 atmosphere.

The sum of the energies, $E_2+E_3+E_4+E_1$, should be equal to E, and a difference greater than the experimental error would indicate that the manner of determining E_2, or E_3, or E_4, is invalid, or that some unknown heat effects accompanied the ignition or the extinction of the flame.

$$E_2+E_3+E_4+E_1=2{,}895.8 \text{ int. joules} \qquad (16)$$

The difference of 0.9 joule between this figure and the value of E is within the experimental error.

In Figure 7 are plotted the values of the "spark," "gas," and "vaporization" energies, in parts per 10,000 of the total energy of a given experiment, against the value obtained for the heat of formation of H_2O in that experiment. This plot shows no trend in the

value obtained for the heat of formation of H_2O with variations in the magnitude of the various energy corrections. In one experiment the "vaporization" energy was 40 times, and in another the "gas" energy was 10 times, the experimental error.

IX. THE EXPERIMENTS AT 25° C.

The first set of experiments was made at 25° C. with the room temperature around 20° to 23° C. These experiments were made between January 18, 1930, and March 1, 1930. The time of energy input on these experiments was measured with a chronograph as explained in Section V, 2, p. 13.

The results of the calibration experiments are shown in Table 1. The symbols heading each column have the significance attached to them in Section VIII, 1, p. 17. The electrical equivalent of the calorimeter system, in international joules per °C., corrected to a common temperature, 25.00° C., and to a common mass of calorimeter water, 3,700.00 g, is given in the next to the last column. The last column gives the deviation from the mean, and the result of the set of calibration experiments gives for the electrical equivalent of this calorimeter system, 15,725.9 international joules per degree at 25.00° C. with 3,700.00 g of water in the calorimeter can.

TABLE 1.—*Calibration experiments, Set I*

Experiment	ΔR	k	u	K	U	$\Delta R_{corr.}$	$\frac{dR}{dt}$	$\Delta t_{corr.}$	Average temperature
	Ohm	*Ohms/min/ohm*	*Ohms/min*	*Ohm*	*Ohm*	*Ohm*	*Ohms/° C.*	*° C.*	*° C.*
1	0.283622	0.002053	0.0000200	0.003410	0.000400	0.279812	0.100876	2.77382	25.14
4	.270009	2052	288	4016	576	.265528	78	2.63217	.07
5	.273817	1968	246	3633	492	.269703	76	2.67361	.12
6	.274047	1945	65	3439	130	.270495	75	2.68149	.16
7	.274931	2034	−6	4153	−12	.270301	77	2.68447	.09
8	.291275	2008	151	3691	302	.287309	78	2.84808	.08
9	.284553	2040	133	3537	266	.280777	76	2.78338	.12
10	.283982	2020	322	3608	644	.279757	77	2.77325	.09
11	.292274	1843	113	3365	226	.288710	77	2.86200	.10
12	.287468	2035	105	3814	210	.283471	78	2.81004	.07
13	.290186	1989	190	3755	380	.286078	78	2.83588	.06

Experiment	e/r (current)	e (voltage)	Time	Electrical energy	Mass of calorimeter water	Electrical equivalent of calorimeter system	Correction to 25.00 ° C.	Correction to 3700.00 g water	Electrical equivalent of calorimeter system [1]	Deviation from mean
	Int. volts/int. ohms	*Int. volts*	*Mean solar seconds*	*Int. joules*	*g*	*Int. joules/° C.*	*Joules/° C.*	*Joules/° C.*	*Int. joules/° C.*	
1	0.939911	65.1998	716.06	43,881.6	3,721.35	15,819.9	0.26	−39.20	15,731.0	5.1
4	.920735	63.8906	704.79	41,460.2	3,705.97	15,751.3	.13	−24.94	26.5	0.6
5	.918639	63.7515	719.86	42,160.6	3,709.42	15,769.2	.22	−39.35	30.0	4.1
6	.937667	65.0632	689.95	42,092.2	3,694.18	15,697.3	.30	24.31	21.9	−4.0
7	.902491	62.6314	749.76	42,379.7	3,714.95	15,787.0	.17	−62.40	24.7	−1.2
8	.967220	67.1024	689.77	44,768.0	3,698.85	15,718.7	.15	4.81	23.6	−2.3
9	.976529	67.7423	660.36	42,717.4	3,695.41	15,706.6	.22	19.17	26.0	.1
10	.975881	67.6959	659.74	43,584.5	3,699.02	15,716.0	.17	4.10	20.3	−5.6
11	.976502	67.7414	674.56	44,621.9	3,667.69	15,591.2	.19	135.00	26.4	.7
12	.959378	66.5390	690.03	44,048.8	3,688.15	15,675.5	.13	49.50	25.2	−.5
13	.959811	66.5880	697.98	44,609.2	3,700.20	15,730.3	.11	−0.34	29.6	3.7
Mean									15,725.9	±2.5

[1] Corrected to 3,700.00 g of water and an average temperature of 25.00° C.

In Table 2 are given the results of the combustion experiments at 25° C. The electrical equivalent, given in the thirteenth column, is obtained by correcting the value 15,725.9 international joules per °C. to the average temperature of the given experiment and to the given mass of water, and then adding to this the heat capacity of one-half the amount of liquid H_2O formed during the experiment. In this table the experiments labeled with a single letter are those in which hydrogen was burned in oxygen, while those having a double letter indicate that oxygen was burned in hydrogen.

The pressure correction to 1 atmosphere is calculated from the thermodynamic equation:

$$w = nRT \log_e \frac{P}{760} \tag{17}$$

where w is the energy in joules to be added; n is taken as the number of moles decrease in gaseous volume; R is the gas constant in joules per degree; T is the absolute temperature; P is the reaction pressure in mm of Hg (mercury barometer readings are corrected to 0° C.). For values of P from 750 to 770 mm, w is calculated to be 5 joules per mole per mm increase in pressure. The pressure in the reaction chamber was determined by adding to the pressure in the room, the pressure drop between the reaction chamber and the final exit tube of the gas line. This latter pressure was determined in separate experiments, for various rates of flow, to be $\Delta P = aL$ where L is the total flow of gas in liters per minute and a is approximately equal to 10 mm /l/min. In most of the experiments, ΔP was 0.5 to 1.0 mm. The pressure in the reaction chamber is given to the nearest mm.

TABLE 2.—*Combustion experiments, Set I*

Experiment	ΔR	k	u	K	U	$\Delta R_{corr.}$	$\frac{dR}{dt}$	$\Delta t_{corr.}$
	Ohm	*Ohms/min/ohm*	*Ohms/min*	*Ohm*	*Ohm*	*Ohm*	*Ohms/° C.*	*° C.*
B	0.290281	0.001904	0.0000135	0.004002	0.000270	0.286009	0.100877	2.83523
C	.298530	2024	121	3153	240	.295135	77	2.92569
D	.295118	1912	65	3213	130	.291776	78	2.89257
E	.279496	2038	143	3685	286	.275525	76	2.73132
F	.281385	2019	−1	3622	−2	.277761	76	2.75349
G	.286564	2071	109	3740	218	.282606	77	2.80149
H	.293339	2045	39	3926	78	.289335	78	2.86817
CC	.293706	1877	266	3634	532	.289540	78	2.87020
DD	.295146	1919	114	3907	228	.291011	78	2.88478

Experiment	Average temperature	Mass of calorimeter water	One-half mass of liquid H_2O formed	Electrical equivalent of calorimeter system	Pressure in reaction chamber	Total energy	"Gas" energy	"Vaporization" energy
	° C.	*g*	*g*	*Int. joules/° C.*	*mm Hg*	*Int. joules*	*Joules*	*Joules*
B	25.10	3,694.65	1.40	15,709.2	754	44,539.2	−13.8	−60.7
C	.11	3,694.56	1.44	15,709.0	754	45,959.7	−10.0	−40.3
D	.07	3,712.03	1.43	15,782.0	762	45,647.4	−8.5	−41.1
E	.15	3,706.02	1.35	15,756.4	753	43,035.8	−14.6	−40.4
F	.14	3,700.88	1.34	15,734.7	766	43,325.3	−36.4	−191.2
G	.11	3,707.08	1.37	15,761.0	763	44,154.3	−22.6	−142.9
H	.08	3,696.04	1.41	15,715.1	761	45,073.6	−12.7	−54.3
CC	.08	3,696.59	1.42	15,717.4	752	45,112.1	−20.3	−22.4
DD	.08	3,689.50	1.42	15,689.1	763	45,259.6	−12.3	−17.3

TABLE 2.—*Combustion experiments, Set I*—Continued

Experiment	"Spark" energy	Reaction energy	Quantity of H_2O formed	$Q_{v,p}$	Temperature correction to 25.00 °C.	Pressure correction to 1 atmosphere	$Q_{25°C.}$, 1 atm.	Deviation from mean
	Joules	*Int. joules*	*Mole*	*Int. joules/mole*	*Joules/mole*	*Joules/mole*	*Int. joules/mole*	
B	11.0	44,602.7	0.156075	285,777	+3	−30	285,750	1
C	7.3	46,002.7	.160959	804	+3	−30	777	28
D	5.5	45,691.5	.159956	650	+2	10	662	−87
E	3.7	43,087.1	.150813	699	+5	−35	669	−80
F	9.2	43,543.7	.152356	802	+5	30	837	88
G	7.3	44,313.1	.155068	766	+3	15	784	35
H	5.5	45,135.1	.157952	752	+3	5	760	11
CC	9.2	45,145.6	.158009	715	+3	−40	678	−71
DD	11.0	45,278.2	.158421	809	+3	15	827	+78
Mean							285,749	±53

X. THE EXPERIMENTS AT 30° C.

It was planned originally to perform all the experiments at 25° C., but after the completion, on about March 1, 1930, of experiment DD, the combustion experiments which were then made gave results which indicated that the calorimetric apparatus was not functioning properly. The first two or three of these odd experiments gave values completely at variance with one another, and far beyond the limits of experimental error. Then three experiments gave concordant results, but were not in agreement with any previous values. Several not very satisfactory calibration experiments were made, and apparently the heat capacity of the calorimeter had changed slightly. During all of these latter experiments it was noted that the ivory supports for the calorimeter can had worn down considerably and unevenly, causing the stirring mechanism to rock the calorimeter can. At this time the calorimeter heater was broken.

About April 1, the calorimeter system was changed. New ivory supports replaced the worn ones. New belting was put in the stirring system. A new cover for the calorimeter can was made. The old heating coil for the calorimeter water was shortened and repaired, and its resistance was now 59.5 as against 69.4 ohms before. The new timing device, described in Section VI, 2, p.14, of this paper, was installed. The jacket temperature was made 31.5° C. and the experiments were conducted at 30° C. because the room temperature was now about 23° to 27° C. All the calibration and combustion experiments at 30° C. were completed in four weeks, beginning April 19, 1930.

The results of the calibration experiments in the new calorimeter system at 30° C. are given in Table 3. The letter S designates experiments of this second set. The agreement of the last four of the five calibration experiments is extraordinarily good. The increased precision in the electrical calibration experiments can be attributed in great part to the use of the new timing device. In calculating the mean of these experiments, the result of S–1 is given a weight of one-third.

TABLE 3.—*Calibration experiments, Set II*

Experiment	ΔR	k	u	K	U	$\Delta R_{corr.}$	$\frac{dR}{dt}$
	Ohm	*Ohms/min/ohm*	*Ohms/min*	*Ohm*	*Ohm*	*Ohm*	*Ohms/° C.*
S-1	0.282183	0.001907	0.0000133	0.004024	0.000266	0.277893	0.100731
S-2	.281962	1927	48	4045	96	.277781	.100730
S-3	.291376	1959	−10	3953	−20	.287443	.100729
S-4	.283590	1926	−29	3995	−58	.279653	.100730
S-5	.291792	1830	−56	3612	−112	.288292	.100727

Experiment	$\Delta t_{corr.}$	Average temperature	e/r (current)	e (voltage)	Time	Electrical energy
	° *C.*		*Int. volts / Int. ohms*	*Int. volts*	*Mean solar seconds*	*Int. joules*
S-1	2.75876	30.01	0.966970	57.5296	780.000	43,390.9
S-2	2.75768	.02	.966781	57.4735	780.000	43,340.2
S-3	2.85363	.08	.982747	58.4275	780.000	44,787.1
S-4	2.77626	.02	.969952	57.6717	780.000	43,632.3
S-5	2.86211	.13	.985700	58.6627	780.000	45,102.6

Experiment	Mass of calorimeter water	Electrical equivalent of calorimeter system [1]	Correction to 30.00° C.	Correction to 3,700.0 g. water	Electrical equivalent of calorimeter system [1]	Deviation from mean
	g.	*Int. joules/° C.*	*Joules/° C.*	*Joules/° C.*	*Int. joules/° C.*	
S-1	3,702.93	15,728.4	0.01	−12.24	15,716.2	4.7
S-2	3,698.71	15,716.2	.02	5.39	21.6	.7
S-3	3,693.47	15,694.8	.08	27.26	22.2	1.3
S-4	3,699.00	15,716.2	.02	4.18	20.4	−.5
S-5	3,709.04	15,758.5	.13	−37.73	20.9	−.0
Mean [2]					15,720.9	±1.0

[1] Corrected to 3,700.00 g of water and an average temperature of 30.00° C.
[2] The result of experiment S-1 has been given a weight of one-third.

The data of the combustion experiments at 30° C. are given in Table 4. Each value is corrected to 25° C. so that comparison can be made with the results of the first set. The temperature and pressure corrections are made as previously explained.

TABLE 4.—*Combustion experiments, Set II*

Experiment	ΔR	k	u	K	U	ΔR_{corr}	$\frac{dR}{dt}$	Δt_{corr}
	Ohms	*Ohms/min/ohm*	*Ohms/min*	*Ohm*	*Ohm*	*Ohm*	*Ohms/° C.*	° *C.*
S-A	0.288111	0.001790	−0.0000123	0.003763	−0.000204	0.284552	0.100729	2.82493
S-B	.295429	1821	−121	3118	−242	.292553	29	2.90436
S-D	.288904	1854	142	3534	284	.285086	29	2.83022
S-E	.283402	1876	3	3553	6	.279843	29	2.77818
S-BB	.287493	1892	244	4155	488	.282850	30	2.80800
S-CC	.281811	1882	81	3997	162	.277652	29	2.75643
S-DD	.284101	1913	111	3834	222	.280045	29	2.78018
S-EE	.294760	1866	156	3557	312	.290891	29	2.88786
S-FF	.287014	1873	12	4117	240	.28273	29	2.80826

TABLE 4.—*Combustion experiments, Set II*—Continued

Experiment	Average temperature	Mass of calorimeter water	One-half mass of liquid H_2O formed	Electrical equivalent of calorimeter system	Pressure in reaction chamber	Total energy	"Gas" energy	"Vaporization" energy
	° C.	g	g	Int. joules/° C.	mm Hg	Int. joules	Joules	Joules
S-A	30.08	3,701.08	1.39	15,731.1	759	44,439.3	−50.7	−70.9
S-B	.07	3,719.05	1.43	15,806.4	763	45,907.5	−46.6	−66.2
S-D	.05	3,693.07	1.40	15,697.8	762	44,428.2	−36.5	−19.1
S-E	.07	3,695.00	1.37	15,705.7	759	43,633.3	−30.1	−19.1
S-BB	.04	3,686.90	1.37	15,671.9	757	44,006.7	−25.3	−99.2
S-CC	.07	3,697.97	1.34	15,617.9	755	43,325.3	−19.9	−133.3
S-DD	.07	3,685.36	1.35	15,665.3	754	43,552.4	1.3	−129.8
S-EE	.07	3,689.40	1.43	15,682.5	759	45,288.9	−20.4	−28.4
S-FF	.05	3,694.37	1.38	15,703.1	760	44,098.4	−28.3	−79.9

Experiment	"Spark" energy	Reaction energy	Quantity of H_2O formed	$Q_{p,t}$	Temperature correction to 25.00° C.	Pressure correction to 1 atm.	$Q_{25^\circ C}$ 1 atm.	Deviation from mean
	Joules	Int. joules	Mole	Int. joules/mole	Joules/mole	Joules/mole	Int. joules/mole	
S-A	11.0	44,549.9	0.155952	285,664	163	−5	285,822	41
S-B	9.2	46,011.1	.161103	600	162	15	777	−4
S-D	9.2	44,474.6	.155688	664	162	10	833	52
S-E	9.2	43,673.3	.152911	612	162	−5	768	−13
S-BB	9.2	44,122.0	.154477	621	161	−15	769	−12
S-CC	9.2	43,469.3	.152190	625	162	−25	762	−19
S-DD	7.3	43,673.6	.152929	581	162	−30	713	−68
S-EE	9.2	45,328.5	.158682	656	162	−5	813	32
S-FF	9.2	44,197.4	.154748	610	162	0	772	−9
Mean							285,781	±28

XI. SUMMARY AND DISCUSSION OF THE RESULTS

In order to compare the results of the experiments of Set I with those of Set II, and later to compare the results of the recomputed data of other investigators, the precision measure used in this paper will be the "95.45% error." This is

$$\text{"error" of the mean} = \pm 2\sqrt{\frac{\Sigma(\bar{x}-x)^2}{n(n-1)}} \qquad (18)$$

where $\Sigma(\bar{x}-x)^2$, is the sum of the squares of the deviations of n experiments. On the ordinary probability theory, the chance that the true average will lie within the above range is 95.45 in 100. The percentage errors of the calibration and combustion experiments in each set are combined by taking the square root of the sum of the squares. In this way, the data of Table 5 are obtained:

TABLE 5

		Number of experiments	"Error"	Combined "error"	Average value	"Error"	"Best" value	"Error"
			Per cent	Per cent				
Set I	Calibration	11	0.013	0.021	285,749	±60	285,775	±34
	Combustion	9	.016					
Set II	Calibration	5	.007	.010	285,781	±28		
	Combustion	9	.008					

The "best" value with its "error" is obtained by weighting the two average values inversely as the squares of their assigned "errors."

An examination of the results also gives the following information:

	Value	Deviation from "best" value
Mean, Set I	285, 749	−28
Median, Set I	285, 760	−17
Mean, Set II	285, 781	+6
Median, Set II	285, 772	−3
"Best" value	285, 775	0

There are several points in connection with the combustion experiments which affect the results to a negligible extent but which should be mentioned here. The first of these is the fact that a small amount of Hg vapor is carried into the region of reaction by the gases flowing through the flow meters. The amount of Hg carried into this region is calculated to be not more than 0.0000006 mole Hg in each experiment.

The second point to consider is the possible formation of H_2O_2 in the experiments in which hydrogen was burned in oxygen. If any H_2O_2 were formed in these experiments, all but a negligible amount must have decomposed into H_2O and O_2 in the reaction vessel because no pronounced differences were found in the results of the two kinds of experiments.[22]

Another point to consider is the fact that the liquid H_2O formed was saturated with O_2 in some experiments and with H_2 in the others. Following a calculation similar to one described by Washburn[23] we find that the heat effect of this saturation with O_2 is about 0.05 joule per mole of H_2O formed, or 1 part in 5,000,000. The effect of saturation with H_2 is of the same order of magnitude.

Still another question to consider is whether the excess gas leaves the calorimeter at the calorimeter temperature. Since the amount of excess gas can be made to approach zero, the error in this regard can also be made negligible. However, since in those experiments in which a large excess of gas was deliberately made to flow through the calorimeter no measurably different results were obtained, the temperature of the exit gases must have been very near to that of the calorimeter.

XII. THE WORK OF PREVIOUS INVESTIGATORS

The reported investigations on the heat of formation of water which have appeared in the past century are listed in Section I, p. 2, of this paper. These data have been critically reviewed by Lewis,[24] by Roth,[25] and by Bichowsky.[26]

Of all the experiments on the heat of formation of water, only those of Schuller and Wartha [27] have attached to them a high measure of

[22] This conclusion is substantiated by the recent work of Riesenfeld and Wassmuth, Zeitschrift für Physikalische Chemie, **149,** p. 140; 1930.
[23] Washburn, Sci. **61,** p. 55; 1925.
[24] Lewis, J. Am. Chem. Soc., **28,** p. 1389; 1906.
[25] Roth, Zeitschrift für Electrochemie, **20,** p. 228; 1920.
[26] This review is unpublished, but the result obtained appears in the International Critical Tables, **5,** p. 176.
[27] See footnote 1 (*i*), p. 2.

reliability and precision. Schuller and Wartha burned oxygen in hydrogen at constant pressure in a glass reaction vessel in an ice calorimeter at such a rate that a mass of about 1.3g of H_2O was formed in three and one-half to four hours. The diminution of volume due to the melting of ice in the calorimeter can (determined from the weight of mercury taken up) served as a measure of the energy evolved. The mass of H_2O formed in the reaction was determined by weighing the reaction vessel before and after the combustion. No significant corrections because of the H_2O formed as a vapor were necessary because of the low vapor pressure of H_2O at 0°C. and because practically a zero amount of excess gas was used in the combustion.

In order to calibrate their calorimeter system in terms of some reproducible unit of energy, Schuller and Wartha dropped a weighed amount of water in a weighed glass container from a steam bath into the ice calorimeter at 0° C. Since the vapor space in the glass container was made negligible, according to Schuller and Wartha, by sealing the vessel at 100° C., these experiments gave the calibration factor in terms of the mean calorie.

The calibration data of Schuller and Wartha are given in Table 6. In this table the original data are italicized, and the other numbers are the writer's recalculations of the data. The results of these five calibration experiments show that 0.015442 g Hg was equivalent to 1 mean calorie.

TABLE 6.—*Calibration experiments of Schuller and Wartha*

Mass of glass container =0.19158 g
Mass of water in container = *.72530* g (in vacuo)

Experiment	Temperature	Grams Hg	Grams Hg corrected to 100° C.	Grams [1] Hg corrected for glass container	Deviation from mean
	° C.				
1	*99.65*	*1.1747*	*1.1788*	1.1208	0.00076
2	*.70*	*40.*	*75*	195	−54
3	*.60*	*47*	*94*	214	136
4	*.95*	*60*	*71*	191	−94
5	*.90*	*62*	*74*	194	−64
Mean				1.12004	±0.00085

[1] It was found that 1 g of the same kind of glass dropped from a steam bath into the ice calorimeter was equivalent to *0.30284* g Hg. The container is therefore equivalent to *0.0580* g Hg.

Osborne, Stimson, and Fiock [28] have determined the relation between the mean calorie, defined as one-one hundredth of the difference in heat content of liquid H_2O, under its own vapor pressure, between 0° and 100° C., and the international joule derived from standards maintained at this bureau. They found that 4.1875 international joules are equivalent to 1 mean calorie. The calibration figures of Schuller and Wartha can now be recalculated in terms of this unit of energy and, as a result,

$$0.0036877 \text{ g Hg} \sim 1 \text{ international joule} \qquad (19)$$

The data of the combustion experiments of Schuller and Wartha are given in Table 7. They report in their paper that certain irreg-

[28] See footnote 17, p. 15.

ularities, unnamed, were present during the course of experiment 3, and they do not use this value in computing their average. Following their advice, the result of experiment 3 is excluded from the present average of their results. This gives the value 285,890 international joules per mole at 25° C. and a constant pressure of 1 atm.

Combining the "error" (as defined in the preceding section, equation (17)), of their calibration experiments with that of the combustion experiments, by taking the square root of the sum of the squares of the percentage "errors," there results for the heat of formation of 1 mole of liquid H_2O (18.0156 g) at 25° C. and 1 atm., from the measurements of Schuller and Wartha, 285,890 ± 235 international joules.

Schuller and Wartha do not mention the magnitude of the "spark" energy used in starting their combustions. A correction for "spark" energy would lower their average value by 15 joules per mole for each joule of spark energy.

TABLE 7.—*Combustion experiments of Schuller and Wartha*

Experiment	Mass of H_2O	Mass of Hg	Pressure in reaction chamber	Total energy	Mole of H_2O	Reaction energy per mole at 0° C., P	Pressure correction to 1 atmosphere	Temperature correction to 25° C.	$Q_{25°C,1atm}$	Deviation from mean
	g	*g*	*mm Hg*	*Int. joules*		*Int. joules/mole*	*Joules/mole*	*Joules/mole*	*Int. joules/mole*	
1	*1.27008*	*74.5310*	*762*	20,210.7	0.070499	286,681	10	−800	285,890	0
2	*1.39350*	*81.7368*	*772*	22,164.9	.077350	553	60	−800	285,810	−80
3	*1.39022*	*81.6133*	*776*	22,131.2	.077168	792	80	−800	(286,070)	.....
4	*1.38082*	*81.0227*	*771*	21,971.1	.076646	657	55	−800	285,910	+20
5	*1.38848*	*81.1946*	*765*	22,017.7	.076793	715	25	−800	285,940	+50
Mean									285,890	±38

The next best existing data on the heat of formation of water are those of Thomsen [29] and of Mixter.[30] Thomsen burned oxygen in hydrogen at constant pressure in a platinum reaction vessel in a calorimeter whose temperature rise was about 4° C. at an average temperature of 18° C. The amount of H_2O formed was determined by weighing the reaction vessel before and after the combustion. The amount of water vapor carried out of the calorimeter by the excess hydrogen was also determined. The temperature rise was measured with a mercury thermometer.

Thomsen calculated the heat capacity of the calorimeter can, reaction vessel, etc., to be 60 calories in terms of the 18° calorie as the unit of energy. The calorimeter contained 2,400 g of water whose average temperature during the experiment was 18° C. As nearly as one can judge from the few details given by Thomsen, the reaction vessel must have been saturated with water vapor before and after each combustion, so that no correction for vaporization of the amount of H_2O vapor required to fill the vessel was necessary. However, a small correction for the amount of H_2O which would vaporize as the temperature of the 500 cm^3 vessel rose from 16° to 20° C. was not made by Thomsen. At the start of the first and second experiments, the amount of H_2O in the platinum reaction vessel was negligible for the purpose of computing the total heat capacity, but

[29] See footnote 1 (*g*), p. 2. [30] See footnote 1 (*n*), p. 2.

at the start of the third experiment there were 4 g of water in the reaction vessel.

The second and third experiments of Thomsen each really consisted of three separate experiments at 18° C., but the amount of H_2O formed was determined only for each group of three, so that only one value results from each group.

The data of Thomsen are given in Table 8, where the original data are italicized. Thomsen makes no mention of the amount of energy in the spark used to ignite the oxygen, nor of the pressure in the reaction chamber. The temperature of the inflowing gases was approximately equal to the average temperature of the calorimeter. The factor 4.1801 is used to convert 18° calories to international joules.[31]

TABLE 8.—*Combustion experiments of Thomsen*

Experiment	Heat capacity of calorimeter system	One-half heat capacity of H_2O formed	Total heat capacity	Corrected temperature rise	Total energy	Mass of H_2O formed	Mole of H_2O	Mass of H_2O carried out of reaction vessel as vapor
	g-cal. $_{18}$/° *C.*	*g-cal.* $_{18}$/° *C.*	*Int. joules/° C.*	*° C.*	*Int. joules*	*g*		*g*
1	*2,460*	1.1	10,288	*3.383*	33,765	*2.129*	0.11818	*0.020*
2	*2,460*	4.0	10,300	*12.321*	126,907	*7.989*	.44345	*.066*
3	*2,464*	4.4	10,318	*13.508*	139,376	*8.810*	.48902	*.089*

TABLE 8.—*Combustion experiments of Thomsen*

Experiment	Mass of H_2O formed as vapor in reaction vessel	"Vaporization" energy	Reaction energy	$Q_{18°\ C.}$	Correction to 25° C.	$Q_{25°\ C.}$	Deviation from mean.
	g	*Joules*	*Int. joules*	*Int. joules/mole*	*Joules/mole*	*Int. joules/mole*	
1	0.0018	53	33,818	286,157	−224	285,930	110
2	.0054	174	127,081	286,573	−224	286,350	530
3	.0054	230	139,606	285,481	−224	285,260	−560
Mean						285,820	±480

The three results are weighted according to the amount of water formed, and the mean value for the heat of formation of liquid H_2O at 25° C. becomes, from Thomsen's data, $285{,}820 \pm 700$ international joules per mole. The error assigned to this value includes an estimated "error" in calibration of 0.10 per cent which in this case comes in the determination of the water equivalent of the calorimeter can, stirrer, reaction vessel, thermometer, etc.

Mixter determined the heat of combustion of hydrogen by exploding the gases in a bomb at constant volume. The heat capacity of the calorimeter system was calculated from that of the parts. The amount of reaction was determined by calculating the mass of hydrogen from its volume, temperature, and pressure. The bomb, whose internal volume was 1,110 cm^3, was filled with hydrogen at 1 atmosphere and oxygen at slightly more than one-half atmosphere.

[31] See Section VII, p. 15.

The data of the 14 experiments performed by Mixter are given in Table 9. The original data are italicized. The heat capacity of the calorimeter parts is calculated from the masses of Cu, Ag, Zn, and Ni, as reported by Mixter, and the heat capacity values given for these substances at 16° to 18° C. in the International Critical Tables.[32] The value given in this table is about 3 joules larger than that calculated by Mixter. One-half the heat capacity of the water formed is used in calculating the total heat capacity of the system, since the average temperature is taken as the temperature of the reaction. The values taken for the heat capacity of water, in international joules per gram, are:[33] 15° C., 4.1834; 16° C., 4.1822; 17° C., 4.1811; 18° C., 4.1801. The mass of H_2O formed as vapor is calculated from the known vapor pressure of H_2O and the final temperature of the calorimeter and the internal volume of the bomb. The values used for the heat of vaporization of water are, in international joules per gram:[34] 2,461 at 15° C. and 2,450 at 20° C. The number of moles of H_2O formed is determined from the molecular weight 2.0156 and the mass of H_2 as calculated by Mixter.

The measured reaction energy at constant volume is corrected (1) from constant volume and the average temperature to constant volume at 17° C., (2) from constant volume at 17° C. to a constant pressure of 1 atm. at 17° C., and (3) to a constant pressure of 1 atm. at 25° C. The first correction is made by taking the temperature coefficient of the heat evolved in the reaction at constant volume as -44 joules per mole per ° C. The second correction is made from the thermodynamic relation, $H=E+PV$, where H is the molal heat content, E is the molal internal energy, V is the molal volume, and P is the pressure. The third correction is made by taking the temperature coefficient[35] of the heat evolved in the reaction at constant pressure as -32 joules per mole per ° C.

In computing the average value from these data, all the experiments of Series I are excluded because of the extremely large deviations in this group. The assigned error for the average value, $285{,}760 \pm 600$ international joules per mole at 25° C., 1 atm., includes an estimated "error" in calibration of 0.10 per cent which arises from the evaluation of the heat capacity of the calorimeter system. Both Mixter, and Roth[36] who recalculated the data of Mixter, included the results of Series I in obtaining their average. After one combustion experiment, Mixter tested for the presence of silver and found about 1 mg. This was due to the formation of silver nitrate from the silver bomb and the nitrogen and oxygen. If an amount of silver nitrate corresponding to 1 mg of silver was formed in all his experiments, then the average value of Mixter as given above should be decreased about 20 joules.

Of the experiments on this problem by other investigators, the results obtained by the early experimenters served admirably well in their day, but are now only landmarks on the road to greater precision and accuracy in these measurements. This group of investigators[37] includes Andrews, Favre and Silbermann, Abria, Grassi, Dulong, and Despretz.

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[32] International Critical Tables, **5**, pp. 85, 86, and 93.
[33] See Section VII, p. 15.
[34] See footnote 17, p. 15.
[35] See footnote 16, p. 15.
[36] See footnote 25, p. 27.
[37] See footnote 1, p. 2.

TABLE 9.—*Combustion experiments of Mixter*

Experiment	Mass of water in calorimeter	Heat capacity of calorimeter water at average temperature	Heat capacity of H_2O formed	Total heat capacity at average temperature [1]	Average temperature of experiment	Corrected temperature rise	Energy	Mass of H_2O formed as vapor	"Vaporization" energy	Reaction energy	Mass of H_2	Mole of H_2O formed	Reaction energy at constant volume, average temperature	Correction to 17° C., constant volume	Q [2 3] 25° C., 1 atm.	Deviation from mean	Series No.
	g	*Int. joules/° C.*	*Joules/° C.*	*Int. joules/° C.*	*° C.*	*° C.*	*Int. joules*	*g*	*Joules*	*Int. joules*	*g*		*Int. joules/mole*	*Joules/mole*	*Int joules/mole*		
1	*1,636.8*	6,844.3	3.6	7,371.3	16.61	*1.773*	13,069.3	0.0164	40.3	13,109.6	*0.09440*	0.046835	279,910	−18	283,250	−2,560	I
2	*1,596.0*	6,673.8	3.5	7,200.7	16.49	*1.823*	13,126.9	168	41.3	13,168.2	*.09266*	.045971	286,450	−22	9,790	3,980	
3	*1,641.0*	6,860.2	3.6	7,387.2	17.55	*1.811*	13,378.2	174	42.7	13,420.9	*.09469*	.046979	285,680	24	9,060	3,250	
4	*1,608.9*	6,725.4	3.4	7,272.2	18.01	*1.785*	12,945.2	178	43.7	12,988.9	*.09202*	.045654	284,500	44	7,900	2,090	
5	*1,591.6*	6,654.2	3.5	7,181.1	17.33	*1.820*	13,069.6	171	42.0	13,111.6	*.09399*	.046631	281,180	15	4,550	−1,260	
6	*1,581.8*	6,614.9	3.6	7,141.8	16.26	*1.853*	132,333.8	161	39.6	13,273.4	*.09489*	.047078	281,950	−33	5,280	−530	
7	*1,604.4*	6,706.4	3.5	7,233.3	18.09	*1.771*	12,810.2	179	43.9	12,854.1	*.09251*	.045897	280,060	48	3,470	−2,340	
8	*1,564.4*	6,542.3	3.5	7,069.2	16.21	*1.853*	12,957.8	160	39.3	12,997.1	*.09294*	.046110	281,870	−35	285,190	−620	
9	*1,586.0*	6,633.0	3.6	7,160.0	16.01	*1.863*	13,339.1	158	38.9	13,378.0	*.09544*	.047351	282,530	−44	5,840	30	
10	*1,641.3*	6,864.4	3.5	7,391.3	15.93	*1.769*	13,075.2	157	38.6	13,113.8	*.09376*	.046517	281,920	−47	5,230	−580	II
11	*1,587.5*	6,637.5	3.5	7,164.4	16.98	*1.841*	13,189.7	168	41.3	13,231.0	*.09452*	.046795	282,750	1	6,110	300	
12	*1,508.9*	6,308.7	3.5	6,835.6	17.10	*1.922*	13,138.0	170	41.8	13,179.8	*.09395*	.046611	282,760	4	6,120	310	
13	*1,558.9*	6,518.4	3.6	7,045.4	16.72	*1.884*	13,273.5	166	40.8	13,314.3	*.09519*	.047227	281,920	−12	5,270	−540	III
14	*1,606.8*	6,717.7	3.4	7,244.5	17.32	*1.786*	12,938.7	171	42.0	12,980.7	*.09227*	.045778	283,560	14	6,930	1,120	
Mean [4]															[5] 285,810	±500	

[1] Heat capacity of calorimeter parts = 523.4 international joules/° C.
[2] Correction from constant volume at 17° C. to constant pressure of 1 atmosphere at 17° C. = +3,614 international joules/mole.
[3] Correction from 17° C., 1 atmosphere, to 25° C., 1 atmosphere = −256 joules/mole.
[4] Series I is not included.
[5] This final mean value requires a further correction of −0.017 per cent, or −50 joules per mole, to take care of the fact that the "vaporization" energy correction used in the table includes the work term RT which is not present when water vaporizes at constant volume. Making this correction, we obtain the value 285,760 international joules per mole, with an average deviation of ±500 joules.

Five experiments on the heat of formation of water were reported by von Than [38] who used an ice calorimeter and obtained an average deviation of about ±0.05 per cent in five combustion experiments. Unfortunately, the calibration data of von Than are so few and so lacking in accuracy as to make the high precision of the combustion experiments practically valueless.

Berthelot [39] reported the result of one experiment. Berthelot and Matignon [40] gave the results of four experiments having an average deviation of ±2,500 joules per mole.

The six results given by Rumelin [41] have an average deviation of ±1,300 joules per mole. The average value of Berthelot and Matignon is about one-half of 1 per cent higher than the usually accepted value while that of Rumelin is lower by nearly the same amount.

The recalculated data of Schuller and Wartha, Thomsen, and Mixter are summarized in Table 10.

TABLE 10

		Number of experiments	"Error"	Combined "error"	Average value	"Error"
			Per cent	*Per cent*		
Schuller and Wartha	Calibration	5	0.080	0.082	285,890	±235
	Combustion	4	.019			
Thomsen	Calibration	0	(.10)	0.24	285,820	±700
	Combustion	3	.220			
Mixter	Calibration	0	(.10)	0.21	285,760	±600
	Combustion	7	.186			

In his recalculation of the data of Schuller and Wartha, Thomsen, and Mixter, Roth obtained for the heat of formation of 18.016 g of water at 18° C., 1 atm., the following values:

Schuller and Wartha	mean cal	68,310
Thomsen	$g=cal._{15}$	68,390
Mixter	do	68,400

Using the factor 4.1875 to convert mean calories into international joules and $\frac{4.185}{1.0004}$ to convert $g=cal._{15}$ into international joules, and correcting the results to 25° C. and 1 atm., and to 18.0156 g of water, one obtains the following values, which are compared with the data recomputed in this paper.

	International joules per mole (18.0156 g) at 25° C. and 1 atmosphere	
	Roth	This paper
Schuller and Wartha	285,820	285,890
Thomsen	285,880	285,820
Mixter	285,920	285,760

[38] See footnote 1 (*h*) and (*j*), p. 2.
[39] See footnote 1 (*k*), p. 2.
[40] See footnote 1 (*l*), p. 2.
[41] See footnote 1 (*n*), p. 2.

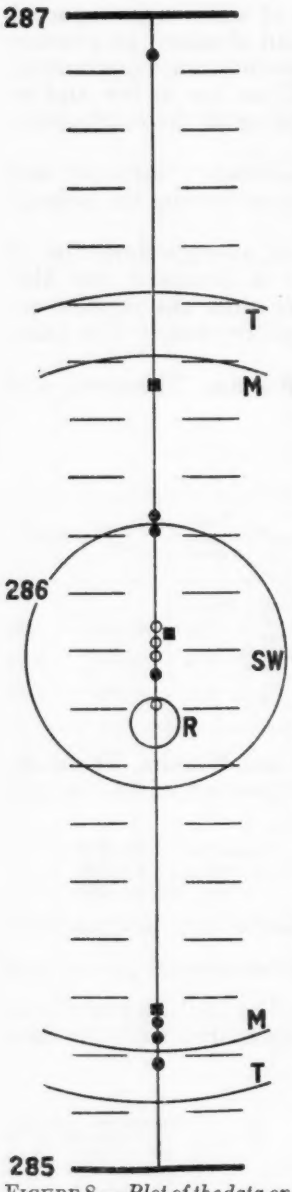

FIGURE 8.—*Plot of the data on the heat of formation of water*

The ordinate scale is in international kilojoules per mole and the data are computed to give the heat of formation of liquid H_2O at 25° C., 1 atmosphere. The points are: ○, Schuller and Wartha; , Thomsen; , Mixter. The small circle shows the assigned limit of error of the value obtained in the present work, while the other circle and arcs show the assigned errors for the recomputed data.

XIII. CONCLUSION

In the foregoing section, the experimental data of three separate groups of experiments on the heat of formation of water have been recalculated. In Figure 8 are plotted the individual values of these experiments: Four of Schuller and Wartha, three of Thomsen, an seven of Mixter. The "best" value of the present investigation is indicated by the small circle, whose radius is a measure of the assigned error, while the other circles and arcs show the corresponding assigned errors of the other investigations.

Figure 9 shows the individual values of the experiments reported in this paper and the "best" value, together with the average value computed from the data of Schuller and Wartha. The radii of the circles measure the assigned errors in each case. All of the individual values of the present experiments fall within the Schuller and Wartha circle, which in turn is completely inclosed by the Thomsen circle and the Mixter circle, as shown in Figure 8.

A liberal estimate of the sum of all errors in this "best" value deduced from the present experiments is ± 40 joules per mole.

The present data give for the heat of formation of 1 mole (18.0156g) of liquid H_2O, according to the equation,

$$H_{2\,(gas)} + 1/2\ O_{2\,(gas)} = H_2O_{(liquid)} \qquad (20)$$

at 25° C. and a constant pressure of 1 atmosphere, the value[42] 285,775 ± 40 international joules. Using the factor 1.0004 to convert international into absolute joules, and $\frac{1}{4.185}$ to convert absolute joules into g-cal_{15}, this value becomes 285,890 ± 40 absolute joules or 68,313 ± 10 g-cal_{15}. The conversion to absolute joules is subject to revision when a more accurate value is obtained for the relation between the international joule derived from standards maintained at this bureau and the absolute joule.

XIV. ACKNOWLEDGMENT

This work was executed under the direction of E. W. Washburn, and the author is

[42] For small changes in temperature and pressure, the heat of formation of water changes, respectively −32 joules per mole per degree increase in temperature, and −5 joules per mole per millimeter increase in pressure.

deeply grateful for his interest, helpful advice, and valued suggestions. Acknowledgments are due to E. F. Mueller for his advice on the calorimetric technic, to F. A. Smith for his aid in designing the reaction vessel, and to the resistance measurements, gas chemistry,

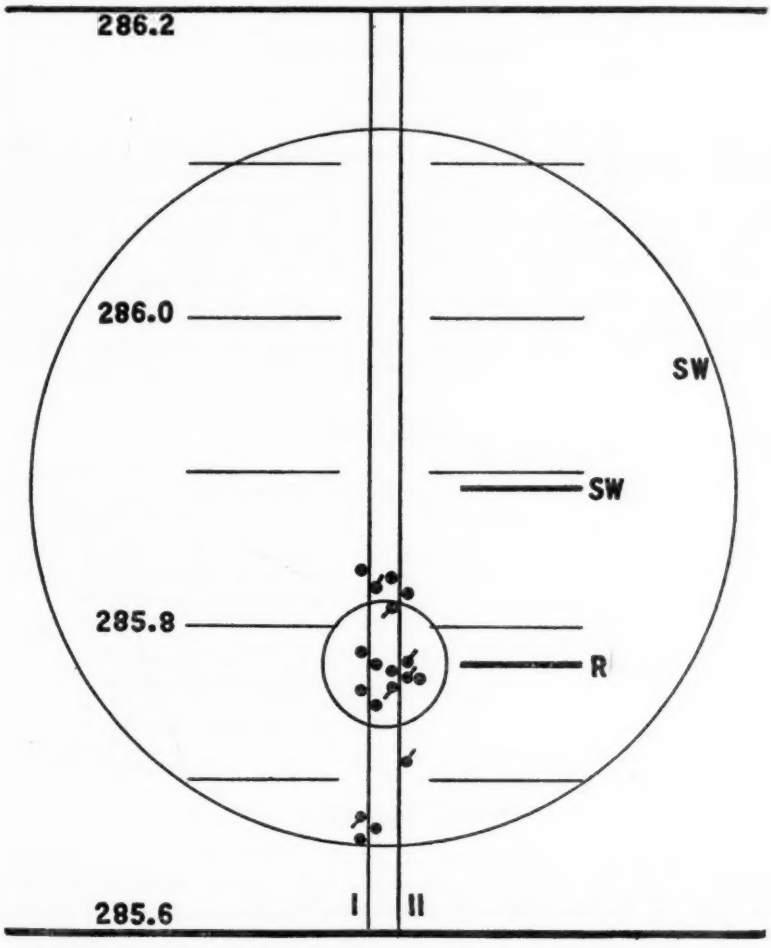

FIGURE 9.—*Plot of the present data on the heat of formation of water*

The ordinate scale gives the heat of formation of liquid H_2O in international kilojoules per mole at 25° C., 1 atmosphere. The O_2 in H_2 experiments are denoted with an appendage. The experiments of Set I are distinguished from those of Set II by the two vertical lines. The average values of Schuller and Wartha and of the present data are shown, together with the "error" circles.

mass, time, thermometry, and standard cell sections of this bureau for their assistance in calibration or analysis. The reaction vessel and gas system were constructed by E. O. Sperling.

WASHINGTON, August 26, 1930.

THE HEATS OF COMBUSTION OF METHANE AND CARBON MONOXIDE

By Frederick D. Rossini

ABSTRACT

With the use of the calorimetric apparatus and procedure employed for determining the heat of formation of water (v. supra p. 1), the heats of combustion of methane and carbon monoxide have been measured.

The heat of combustion of CH_4 to form liquid H_2O and gaseous CO_2 is found to be $889,700 \pm 300$ international joules per mole at 30° C. and a constant pressure of 1 atmosphere, which is equivalent to $890,160 \pm 300$ international joules per mole at 25° C. and 1 atm.

The heat of combustion of CO to form CO_2 is found to be $282,925 \pm 120$ international joules per mole at 30° C. and a constant pressure of 1 atm., which is equivalent to $282,890 \pm 120$ international joules per mole at 25° C. and 1 atm.

For comparison with the older work, see Figures 1 and 2.

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I. INTRODUCTION

The heats of formation of methane and carbon monoxide are computed from their heats of combustion because of the difficulties inherent in the problem of measuring the heat effect of their synthesis from or decomposition into the elements. Accurate values of the heats of formation of methane and carbon monoxide are particularly desirable at this time because industrial syntheses of many useful compounds involve one or both of these gases, and a knowledge of the heat effect of a given reaction permits calculation of the change of the equilibrium with temperature.

The usually accepted values for the heats of combustion of methane and carbon monoxide are based primarily upon the measurements made over 50 years ago by Thomsen. Because of the comparatively large uncertainty (one-fourth to one-third per cent) attached to Thomsen's average values, and because calorimetric measuring apparatus, methods, and devices have improved greatly in accuracy and precision since his time, it was desirable that new determinations be made.

II. APPARATUS AND CALORIMETRIC PROCEDURE

It was found that the calorimetric apparatus which was used in this laboratory to determine the heat of formation of water [1] could be used, without alteration, for burning methane and carbon monoxide in oxygen. The reaction vessel and other apparatus have been described in detail.[1]

The calorimetric procedure in the experiments involving combustion of methane and carbon monoxide was exactly similar to that employed in the combustion of hydrogen and the experiments here reported were carried out immediately after the completion of the latter combustions.

The data from the calibration experiments at 30° C., listed as Set II in the experiments on hydrogen, were used in conjunction with the combustion experiments on methane and carbon monoxide.

While the curves showing the variation of the calorimeter temperature with time in the combustion experiments on hydrogen were practically identical with those in the calibration experiments, those for the combustion experiments involving methane and carbon monoxide were somewhat different. In the calibration experiments, the temperature rise of about 2.8° C. occurred in 12 minutes, whereas for the combustion experiments on methane and carbon monoxide it was 2.8° C. in 10 minutes and 1.3° C. in 12 minutes, respectively. Since, however, detailed observations in the "fore" and "after" periods were made in each experiment, and since the resistance coils in the thermometer bridge were accurately calibrated, the determination of the true temperature rise in each experiment can be in error by only a negligible amount.

III. MOLECULAR WEIGHTS, CONSTANTS, UNITS, AND FACTORS

The atomic weights of O, H, and C are taken as 16.000, 1.0078, and 12.000, respectively.[2]

For the reaction between CH_4 and O_2 to form liquid H_2O and gaseous CO_2, ΔC_p is taken as 93 joules per mole per degree,[3] that is, the heat evolved in the reaction at constant pressure decreases 93 joules per mole per degree.

For the reaction between CO and O_2 to form CO_2, ΔC_p is taken as -7 joules per mole per degree.[3] The heat evolved in this reaction at constant pressure increases 7 joules per mole per degree.

The correction to 1 atmosphere pressure is made by the use of the thermodynamic equation.

$$w = n\mathbf{R}T \log_e \frac{P}{760} \tag{1}$$

where n is the number of moles decrease in gaseous volume, $\mathbf{R}$ is the gas constant in joules per degree, T is the absolute temperature, P is the pressure in mm of Hg. For the combustion of methane, w is taken as -6.7 joules per mole per mm increase in pressure, while for the conbustion of carbon monoxide w is -1.7 joules per mole

[1] Rossini, B. S. Jour. Research, **6**, p. 1; 1931.
[2] Baxter, 1930 Report of the Committee on Atomic Weights, J. Am. Soc., **52**, p. 861; 1930.
[3] International Critical Tables, **5**, p. 80.

per mm increase in pressure. These corrections are strictly valid only for small changes in pressure. The pressures in the reaction chamber for the combustion experiments are given in Tables 4 and 8.

The unit of energy and all other constants, units, and factors are the same as those given in the previous paper.[4]

IV. METHANE

1. CHEMICAL PROCEDURE

The methane used in this investigation, obtained through the courtesy of the Fixed Nitrogen Research Laboratory, had been prepared synthetically from carbon monoxide and hydrogen and was specially purified by the Du Pont Ammonia Co. The purifying procedure included a fractional distillation to remove other hydrocarbons, hydrogen, and carbon monoxide.

Before entering the reaction vessel, the methane passed successively through tubes containing (1) "ascarite" (sodium hydroxide-asbestos mixture) for removing CO_2 and other acidic oxides, (2) "dehydrite" ($Mg(ClO_4)_2.3H_2O$) for removing water vapor, and (3) P_2O_5 for removing the last traces of H_2O.

The ratio of carbon to hydrogen in the methane was determined by burning the gas in the reaction vessel in an excess of oxygen and absorbing the H_2O in "dehydrite" and the CO_2 in "ascarite." For this absorption, two glass-stoppered U-tubes, similar to that used in the hydrogen combustions, were used in series. The first tube contained "dehydrite" and P_2O_5, and the second "ascarite" and P_2O_5. The first tube absorbed only the H_2O while the second absorbed all the CO_2. Because of the large amount of heat evolved when "ascarite" absorbs CO_2, the second tube was placed in a beaker of water.

The procedure employed in determining the mass of H_2O formed has been described in detail.[5]

The mass of CO_2 absorbed was determined in the same manner. When "ascarite" absorbs CO_2, two reactions occur:

$$2NaOH\ (\text{hydrated}) + CO_2 = Na_2CO_3\ (\text{hydrated}) + H_2O\ (\text{water of hydration}) \quad (2)$$

$$NaOH\ (\text{hydrated}) + CO_2 = NaHCO_3 + H_2O\ (\text{water of hydration}) \quad (3)$$

The molecular volumes[6] were taken as follows: $NaHCO_3$, 38.2 cm^3; NaOH (hydrated), 18.8 cm^3 + 15.6 cm^3 for each mole of water of hydration; Na_2CO_3, 41.8 cm^3 + 15.6 cm^3 for each mole of water of hydration. The increase in volume of the "ascarite" is 0.45 ± 0.02 cm^3 per gram of CO_2 absorbed. Following a calculation similar to one already described,[7] the mass of CO_2 absorbed becomes, when the absorber is filled with oxygen at 25° C. and 1 atmosphere.

$$m_{(CO_2)} = (1.00000 + 0.00059 - 0.00014) \times \Delta m = 1.00045 \Delta m \quad (4)$$

where m is the mass of the brass weights. The uncertainty in this factor is not more than 2 in 100,000. When the absorber is filled

[4] See footnote 1, p. 38.
[5] See footnote 1, p. 38.
[6] Calculated from densities and molecular weights given in International Critical Tables, 1, pp. 150, 151.
[7] See footnote 1, p. 38.

with hydrogen, as it was in some experiments, the mass of CO_2 is obtained from the following equation:

$$m_{(CO_2)} = (1.00000 + 0.00004 - 0.00014) \times \Delta m = 0.99990 \Delta m \quad (5)$$

The results of four determinations of the ratio of H_2O to CO_2 are given in Table 1. When the methane was burned in oxygen according to the equation

$$CH_4 + 2O_2 = 2H_2O + CO_2 \quad (6)$$

it was found that the ratio of half the moles of H_2O to the number of moles of CO_2 formed was 0.99885 ± 0.00019.

TABLE 1.—*Ratio of H_2O to CO_2 in the combustion products of methane*

Experiment	Mole of H_2O	Mole of CO_2	Ratio: $\frac{1/2 \text{ moles } H_2O}{\text{moles } CO_2}$	Deviation from mean
1	0.125614	0.062886	0.99875	−0.00010
2	.111594	.055855	.99896	.00011
3	.081449	.040761	.99911	.00026
4	.115400	.057783	.99857	−.00028
Mean			.99885	±.00019

The excess of CO_2 could be explained by the presence in the methane of a small amount of CO. Accordingly, the methane was analyzed directly for CO by the gas chemistry section of this bureau with the aid of the I_2O_5 apparatus developed by them.[8] The results of their analyses are given in Table 2. While the ratio of H_2O to CO_2 indicated the presence of CO to the extent of (0.115 ± 0.019) per cent, the direct analyses gave (0.1219 ± 0.0013) per cent. For the purpose of correcting the calorimetric data for the amount of CO present, this was taken as 0.122 per cent.

TABLE 2.—*Determination of CO in the methane*

Experiment	Observed volume of CH_4	Observed volume of $Na_2S_2O_3$ solution	Calculated volume of CO	CO	Deviation from mean
	ml	*ml*	*ml*	*Per cent*	
1	486.4	10.80	0.5915	0.1215	−0.0004
2	488.0	11.05	.6050	.1239	.0020
3	484.0	10.64	.5830	.1204	−.0015
Mean				.1219	±.0013

In the combustion experiments on methane, the amount of reaction was determined from the mass of H_2O formed.

Since the determination of the ratio of H_2O to CO_2 in the products of combustion of the methane gas showed that, exclusive of the 0.122 per cent of CO, the ratio of the number of C atoms to one-fourth the number of H atoms was 1.0000 ± 0.0002, the amount of H_2 or

[8] (*a*) This apparatus and method are described by J. H. Eiseman in the Gas Chemists' Hand Book, p. 289; 1929. American Gas Association, New York. (*b*) Lamb, Bray, and Frazer, Ind. Eng. Chem., **12**, p. 213; 1920.

C_2H_6 which could be present in the methane without being detected was about 0.04 or 0.06 mole per cent, respectively. The amount of any hydrocarbon other than C_2H_6 which could have been present is less than 0.06 mole per cent. The following table shows the per cent error in the heat of combustion of methane caused by undetected amounts of these substances:

Impurity	Possible undetected amount	Error in heat effect caused by undetected amount
	Mole per cent	*Per cent*
H_2	0.04	0.013
C_2H_6	.06	.014
C_2H_4	.02	.011
C_2H_2	.007	.014
C_3H_8	.03	.014

The proper ratio of C to H could have been maintained by suitable amounts of hydrogen and other hydrocarbons than methane. The following table shows the amount of such impurities required to produce an error of 0.01 per cent in the heat of combustion of methane.

Impurity	Amount of impurity required to produce an error of 0.01 per cent in the heat effect
	Mole per cent
$C_2H_6+H_2$	0.39
$C_2H_4+2H_2$	.14
$C_2H_2+3H_2$	.094
$C_3H_8+2H_2$	.27

2. CORRECTION EXPERIMENTS

As in the combustion experiments with hydrogen, the calorimetric experiments where methane was burned in oxygen had associated with them in addition to the heat of the given reaction, three sources or sinks of energy which were not present in the calibration experiments: (1) the energy given to the calorimeter by the sparking operation (2) the energy required to bring the inflowing gases to the temperature of the calorimeter, and (3) the energy of vaporization of the H_2O not condensed to liquid.

The "spark" energy, determined as in the hydrogen experiments, was found to be 1.60 joules per second. The "gas" energy and the "vaporization" energy were calculated as before.

An experiment involving three separate ignitions and extinctions of the methane flame was made to test the validity of the energy corrections. The data obtained in this experiment are given in Table 3. The measured amount of energy was 3,124.3 international joules, while the calculated sum of the "spark," "gas," and "vaporization" energies, and the energy liberated by the combustion of the CH_4, is 3,124.8 international joules. The difference of 0.5 joule is well within

the experimental error. The heat effect of the solution of CO_2 in the water formed is calculated to be negligible (1 or 2 parts per 100,000).

TABLE 3.—*Correction experiment for combustion of methane*

Electrical equivalent of calorimeter	int. joules/° C	15632. 6
Corrected temperature rise	° C	0. 19986
E, the total energy	int. joules	3124. 3
Moles of CH_4 burned		0. 035278
E_1, "spark" energy	joules	28. 8
E_2, "gas" energy	do	−5. 2
E_3, "vaporization" energy	do	−38. 3
E_4, Heat of combustion of CH_4(+0.122 per cent CO)	int. joules	3139. 5
$E_1+E_2+E_3+E_4$	do	3124. 8

3. COMBUSTION EXPERIMENTS

The experiments on the combustion of methane were performed in the same manner as were the hydrogen combustions. The results are given in Table 4. The result of experiment A is not included in obtaining the average. The "error" of the mean [9] is calculated from the equation

$$\text{"Error" of the mean} = \pm 2\sqrt{\frac{\Sigma(\bar{x}-x)^2}{n(n-1)}} \tag{7}$$

when $\Sigma(\bar{x}-x)^2$ is the sum of the squares of the deviations of n experiments. The value obtained for the heat of the reaction

$$CH_{4(gas)} + 2O_{2(gas)} = 2H_2O_{(liquid)} + CO_{2(gas)} \tag{8}$$

is 889,700 ± 270 international joules per mole at 30° C. and a constant pressure of 1 atmosphere.

4. DATA OF PREVIOUS INVESTIGATORS

The heat of combustion of methane was measured by Andrews [10] in 1848, Favre and Silbermann [11] in 1852, Thomsen [12] in 1880, and Berthelot [13] in 1881.

TABLE 4.—*Experiments on combustion of methane*

Experiment	ΔR	k	u	K	U	$\Delta R_{corr.}$	$\frac{dR}{dt}$	$\Delta t_{corr.}$
	Ohm	*Ohm/min/ohm*	*Ohm/min*	*Ohm*	*Ohm*	*Ohm*	*Ohm/° C.*	*° C.*
A	0. 291604	0. 001873	−0. 0000063	0. 002721	−0. 000101	0. 288984	0. 100730	2. 86890
B	. 291832	1899	63	2552	101	. 289179	30	2. 87083
C	. 288904	1867	37	3468	59	. 285377	31	2. 83306
D	. 287126	1892	106	2722	170	. 284235	30	2. 82173
E	. 293829	1903	268	2725	429	. 290675	30	2. 88568
F	. 290884	1888	58	2619	93	. 288172	30	2. 86084

[9] See footnote 1, p. 28.
[10] Andrews, Phil. Mag., **32**, p. 326; 1848.
[11] Favre and Silbermann, Annales chim. phys., **34**, p. 426; 1852.
[12] Thomsen, (*a*) Berichte, **13**, p. 1323; 1880. (*b*) "Thermochemische Untersuchungen," **4**, p. 48. J. A. Barth, Leipzig; 1886.
[13] Berthelot, Annales chim. phys., **28**, p. 178; 1881.

TABLE 4.—*Experiments on combustion of methane*—Continued

Experiment	Average temperature	Mass of calorimeter water	One-half mass of liquid H_2O formed	Electrical equivalent of calorimeter system	Pressure in reaction chamber	Total energy	"Gas" energy	"Vaporization" energy
	° C.	g	g	Int. joules/° C.	mm Hg	Int. joules	Joules	Joules
A	30.02	3,687.80	0.86	15,673.6	762	44,966.0	33.8	249.6
B	30.03	3,692.00	.90	15,691.3	761	45,047.1	9.1	168.5
C	30.01	3,686.63	.88	15,668.8	759	44,390.7	15.5	202.5
D	30.03	3,684.10	.88	15,658.2	753	44,183.5	6.9	158.8
E	30.02	3,674.80	.89	15,619.5	750	45,072.9	11.5	155.1
F	30.02	3,689.43	.88	15,680.7	761	44,860.0	23.8	160.7

Experiment	"Spark" energy	Reaction energy	Moles of CH_4	$Q_{D,t}$	Correction to 30° C.	Correction to 1 atmosphere	Correction for 0.122% CO	$Q_{30°\,C.\ 1atm.}$	Deviation from mean
	Joules	Int. joules		Int. joules/mole	Joules/mole	Joules/mole	Joules/mole	Int. joules/mole	
A	16	45,233.4	0.0507360	891,544	−2	+13	−345	(891,210)	
B	9.6	45,215.1	.0507829	890,361	−3	7	−345	890,020	323
C	30.4	44,578.3	.0501019	889,753	−1	−7	−345	889,400	−297
D	9.6	44,339.6	.0498038	890,285	−3	−47	−345	889,890	193
E	9.6	45,229.9	.0508121	890,141	−2	−67	−345	889,727	30
F	9.6	45,034.9	.0506131	889,788	−2	7	−345	889,448	−249
Mean								889,700	±218

Electrical equivalent of calorimeter system with 3,700.00 g water at 30° C.=15,720.9 international joules per ° C.

Because of the large amounts of impurities present in the methane burned by Andrews and by Favre and Silbermann, and because of the fact that lack of suitable calibration of their calorimeter systems makes sufficiently accurate translation of their data into modern energy units practically impossible, their results are not reviewed here.

Thomsen burned methane in a reaction vessel at constant pressure. The amount of reaction was determined from the CO_2 formed by absorption in KOH solution. The results of the 11 experiments reported by Thomsen, corrected to 30° C. (presumably at 1 atmosphere), and to international joules per mole, are given in Table 5. Computing the "error" of the average by equation (5), the result of Thomsen's data becomes 886,380 ± 2,840 international joules per mole. This includes an estimated error of 0.1 per cent in the calibration of his calorimeter; that is, in his calculation of the heat capacity of his calorimeter.

Berthelot reported the results of three experiments in which methane was exploded with oxygen in a bomb at constant volume. The amount of reaction was determined from the mass of methane, computed from its volume, pressure, and temperature. The data of Berthelot, corrected to international joules per mole at 30° C. and 1 atmosphere, are given in Table 6. The average of these data is 891,700 ± 9,000 international joules per mole. The "error" includes an estimated error of 0.1 per cent in calibration.

The individual values of the experiments by Thomsen and by Berthelot, together with the present data, are shown in Figure 1. The circles or arcs are drawn with radii equal to the assigned

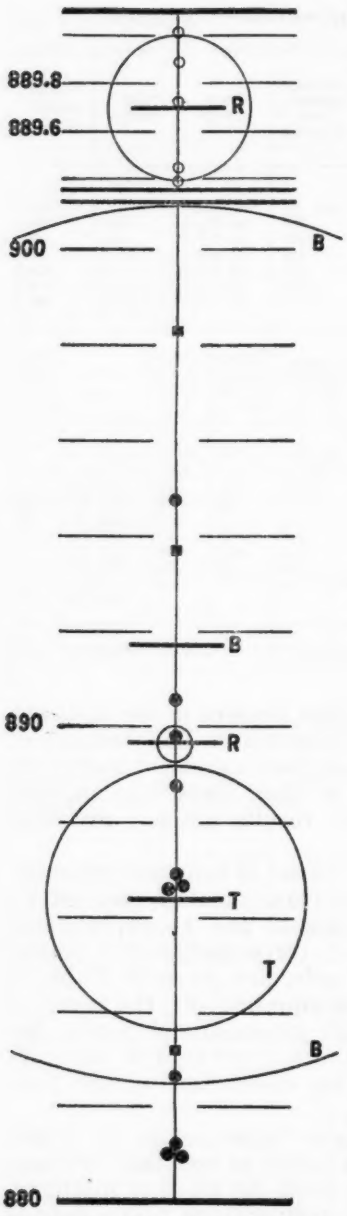

FIGURE 1.—*Plot of the data on the heat of combustion of methane*

The ordinate scale gives the heat of combustion of methane in international kilojoules per mole at 30° C., and 1 atmosphere. The points designate the data of the various investigators: ■, Berthelot; ●, Thomsen; ○, Rossini.

"errors." The upper section of Figure 1 shows a magnified view of that portion of the lower scale in which fall the values obtained in this investigation.

TABLE 5.—*Results obtained by Thomsen on the combustion of methane*

Experiment	$Q_{30°\,C.,\,1\,atm.}$	Deviation from mean
	Int. joules per mole	
1	886, 770	390
2	888, 770	2, 390
3	881, 020	−5, 360
4	889, 820	3, 440
5	886, 890	510
6	882, 660	3, 720
7	881, 240	−5, 140
8	886, 680	300
9	881, 080	−5, 300
10	894, 750	8, 370
11	890, 540	4, 170
Mean	886, 380	±3, 550

TABLE 6.—*Results obtained by Berthelot on the combustion of methane*

Experiment	$Q_{30°\,C.,\,1\,atm.}$	Deviation from mean
	Int. joules/mole	
1	893, 700	2, 000
2	898, 300	6, 600
3	883, 200	−8, 500
Mean	891, 700	±5, 700

V. CARBON MONOXIDE

1. CHEMICAL PROCEDURE

The carbon monoxide used in this investigation had been prepared by the Fixed Nitrogen Research Laboratory.[14] The gas was made by decomposing formic acid with phosphoric acid at 170° C,. according to the reaction.

$$HCOOH = CO + H_2O \qquad (9)$$

The product was purified from traces of undecomposed acid with sodium hydroxide solution. Scrubbings with potassium hydroxide solution, and passage through a cold trap at −80° C., preceded

[14] Thompson, Ind. Eng. Chem., **21**, p. 389; 1929.

the compression of the gas into steel cylinders. A possible small impurity of hydrogen might arise from the reaction

$$HCOOH = CO_2 + H_2 \tag{10}$$

Because of its contact with the iron of the steel cylinder in which it was kept, the carbon monoxide contained, besides moisture, a small amount of iron carbonyl whose presence is easily detected by the yellow color it imparts to the flame. This iron carbonyl was decomposed into Fe and CO by passage through a tube filled with preignited asbestos at a temperature of about 500° C.

This process of eliminating the iron carbonyl resulted in the occurrence of two other reactions, as follows:

$$2CO = C + CO_2 \tag{11}$$

$$H_2O + CO = CO_2 + H_2 \tag{12}$$

The C was deposited in the asbestos while the CO_2 formed, along with that which was originally in the carbon monoxide, was removed by passage through a tube containing "ascarite." The H_2 formed in the second reaction between H_2O and CO, remained in the carbon monoxide. The amount of H_2 was determined by absorbing, in separate U-tubes, the CO_2 and H_2O formed, as described in the preceding section under the determination of the ratio of C to H in CH_4. Two determinations of the amount of H_2 in the carbon monoxide entering the reaction vessel gave, respectively, 0.105 and 0.101 mole per cent. This consisted of the H_2 formed in the hot tube, together with a small amount (about 0.04 per cent) which was originally in the carbon monoxide.

In determining the amount of CO burned in the combustion experiments, the mass of CO_2 (plus the small amount of H_2O formed) was obtained, the correction to vacuum being made with the aid of equations (4) and (5). From this mass was subtracted the amount of H_2O absorbed (0.042 weight per cent), and the result divided by 44.000, the molecular weight of CO_2, to give the number of moles of CO burned. The measured reaction energy was decreased by an amount corresponding to the combustion of the 0.103 mole per cent of H_2 to form gaseous H_2O.

2. CORRECTION EXPERIMENTS

Pure dry carbon monoxide is difficult to ignite, but the presence of H_2 or H_2O greatly decreases this difficulty. The presence of the 0.1 per cent H_2 in the carbon monoxide was advantageous in this regard, but even so, it was found that a much longer time of sparking (5 to 30 seconds) was required to ignite the carbon monoxide than was necessary for either the hydrogen or the methane. This accounts for the failure to obtain the expected greater precision in the combustion experiments on carbon monoxide.

The "spark" energy, determined as before, was now found to be 1.28 joules per second. The "gas" energy was calculated as in the previous experiments. In order to check the validity of the "spark" and "gas" energy corrections, three separate experiments were

performed. The results are given in Table 7. The difference between the measured energy, E, and the computed sum of the energies, $E_1+E_2+E_4$, are with one exception, well within the experimental error.

TABLE 7.—*Correction experiments for combustion of carbon monoxide*

	Experiment		
	1	2	3
Electrical equivalent of calorimeter ..... int. joules °C..	15621.3	15621.3	15621.3
Corrected temperature rise ..... °C..	0.05167	0.05041	0.03078
E, total energy ..... int. joules..	*807.1*	*787.5*	*480.8*
Mole of CO burned	0.0027020	0.0025221	0.0014771
E_1, "spark" energy ..... joules..	42.2	80.6	64.0
E_2, "gas" energy ..... do....	−1.5	−1.5	−1.5
E_4, heat of combustion of CO (+0.103 per cent H_2) ..... int. joules..	765.2	714.3	418.3
$E_1+E_2+E_4$ ..... do....	*805.9*	*793.4*	*480.8*
Difference ..... joules..	−1.2	+5.9	0.0

3. COMBUSTION EXPERIMENTS

The data of the combustion experiments involving carbon monoxide are given in Table 8. The electrical equivalent of the calorimeter is 0.9 joule per degree less than in the previous experiments because of the removal of 0.24 g of copper.

The average of the eight experiments gives for the heat of combustion of CO, according to the equation

$$CO_{(gas)}+1/2O_{2(gas)}=CO_{2(gas)} \qquad (13)$$

$282,925 \pm 100$ international joules per mole at 30° C. and a constant pressure of 1 atm. The "error" is calculated according to equation (7).

TABLE 8.—*Experiments on combustion of carbon monoxide*

Experiment	ΔR	k	u	K	U	$\Delta R_{corr.}$	$\frac{dR}{dt}$	$\Delta t_{corr.}$
	Ohm	*Ohm/min/ohm*	*Ohm/min*	*Ohm*	*Ohm*	*Ohm*	*Ohms/° C.*	*° C.*
A	0.134528	0.001858	0.0000115	0.001538	0.000230	0.132760	0.100730	1.31798
B	.111010	1853	65	1857	130	.109023	23	1.08240
C	.127761	1855	197	2755	493	.124513	31	1.23609
D	.134972	1915	139	1643	278	.133051	30	1.32087
E	.130186	1933	241	1786	482	.127918	30	1.26991
F	.134312	1881	117	1550	234	.132528	30	1.31568
G	.135181	1809	251	1656	502	.133049	30	1.32085
H	.118339	1875	28	2036	56	.116247	32	1.15402

Experiment	Average temperature	Mass of calorimeter water	Electrical equivalent of calorimeter system	Pressure in reaction chamber	Total energy	"Gas" energy	"Spark" energy	Reaction energy
	° C.	*g*	*Int. joules/° C.*	*Mm Hg*	*Int. joules*	*Joules*	*Joules*	*Int. joules*
A	30.04	3,688.32	15,671.3	760	20,654.5	11.8	10.2	20,656.1
B	30.28	3,683.95	15,652.7	754	16,942.5	8.5	15.4	16,935.6
C	29.99	3,682.15	15,655.5	750	19,351.6	14.1	32.0	19,333.7
D	30.02	3,675.85	15,619.2	750	20,630.9	9.7	32.0	20,608.6
E	30.04	3,686.59	15,664.0	749	19,891.9	12.9	48.6	19,856.2
F	30.02	3,685.95	15,661.4	750	20,605.4	8.3	28.1	20,585.6
G	30.02	3,681.75	15,643.8	753	20,663.1	17.0	35.9	20,644.2
H	29.96	3,681.85	15,644.3	753	18,053.8	9.7	23.1	18,040.4

TABLE 8.—*Experiments on combustion of carbon monoxide*—Continued

Experiment	Moles of CO	$Q_{p,t}$	Correction to 30° C.	Correction to 1 atmosphere	Correction for 0.103 per cent H_2	$Q_{30°\,C.,\,1\,atm.}$	Deviation from mean
		Int. joules/mole	*Joules/mole*	*Joules/mole*	*Joules/mole*	*Int. joules/mole*	
A	0.0729688	283,077	0	0	−249	282,828	−97
B	.0597962	283,223	−2	−10	−249	282,962	37
C	.0682694	198	0	−17	−249	282,932	7
D	.0728097	048	0	−17	−249	282,782	−143
E	.0700779	345	0	−18	−249	283,078	153
F	.0727235	068	0	−17	−249	282,803	−122
G	.0729188	113	0	−12	−249	282,852	−73
H	.0636511	426	0	−12	−249	283,165	240
Mean						282,925	± 109

Electrical equivalent of calorimeter system with 3,700.00 g water at 30° C.=15,720.0 international joules per ° C.

4. DATA OF OTHER INVESTIGATORS

The heat of combustion of carbon monoxide was measured by Dulong [15] in 1838, Andrews [16] in 1848, Favre and Silbermann [17] in 1852, Berthelot [18] in 1878 and 1880, and Thomsen [19] in 1880. As before, only the results of Thomsen and of Berthelot are compared with those of the present investigation.

Thomsen reported the results of 10 experiments in which carbon monoxide was burned in oxygen at constant pressure. The results of Thomsen, corrected to international joules per mole at 30° C. (presumably at 1 atm.), are given in Table 9. The average value is 284,140 ± 710 international joules per mole. The assigned "error" includes an estimated error in calibration of 0.1 per cent and is calculated by equation (7).

TABLE 9.—*Results obtained by Thomsen on the combustion of carbon monoxide*

Experiment	$Q_{,30°\,C.,\,1\,atm.}$	Deviation from mean
	Int. joules/mole	
1	284,680	580
2	284,120	20
3	284,160	60
4	282,580	−1,520
5	285,110	1,010
6	283,980	−120
7	282,250	−1,850
8	283,930	−170
9	285,630	1,530
10	284,590	490
Mean	284,140	±735

Berthelot reported two values for constant pressure and two for constant volume. These data, corrected to international joules per mole at 30° C., and 1 atm., are given in Table 10. The average value with its assigned "error" is 284,800 ± 2,000 international joules per mole.

[15] Dulong, Comptes rendus, **7,** p. 871; 1838.
[16] Andrews, Phil. Mag., **32,** p. 325; 1848.
[17] Favre and Silbermann, Annales chim. phys., **34,** p. 405; 1852.
[18] (*a*) Berthelot, Annales chim. phys., **13,** p. 1; 1878; (*b*) **20,** p. 255; 1880.
[19] Thomsen, "Thermochemische Untersuchungen," II, p. 288, J. A. Barth, Leipzig, 1886.

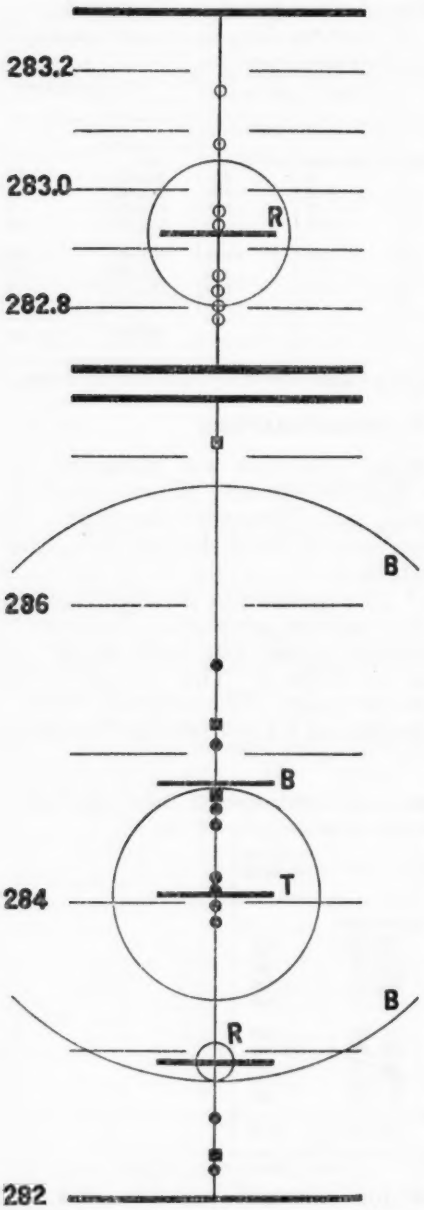

FIGURE 2.—*Plot of the data on the heat of combustion of carbon monoxide*

The ordinate scale gives the heat of combustion of carbon monoxide in international kilojoules per mole at 30° C. and 1 atmosphere. The points designate the data of the various investigators: Berthelot; ●, Thomsen; ○, Rossini.

TABLE 10.—*Results obtained by Berthelot on the combustion of carbon monoxide*

Experiment	$Q_{30°\,C.,\,1\,atm.}$	Deviation from mean
	Int. joules/mole	
1	285, 200	400
2	284, 700	−100
3	282, 300	−2, 500
4	287, 100	2, 300
Mean	284, 800	±1, 300

In Figure 2 are shown the individual values of Thomsen and of Berthelot, together with the data of the present investigation. The circles or arcs are drawn with radii equal to the assigned "errors." The upper part of Figure 2 shows a magnified view of that part of the lower scale in which fall the values of the present work.

VI. CONCLUSION

On comparing the data of Thomsen and of Berthelot on the heats of combustion of methane and carbon monoxide with the data obtained in the present investigation, one finds that (1) the average values of Berthelot, plus or minus the assigned "errors," are in agreement with the values obtained in the present work and (2) that the average values of Thomsen, both for methane and carbon monoxide, have assigned to them "errors" which are too small (made so by the comparatively large number of observations) for agreement with the present data. This latter fact implies the existence of some systematic error in the measurements of Thomsen—of opposite sign in the two sets of data.

Conservative estimates of the uncertainty, from all causes, in the average values of the heats of combustion of methane and carbon monoxide as determined from the present data are, respectively, ±300 and ±120 joules per mole.

From the data of the present investigation the heat of combustion of CH_4 in O_2 to form liquid H_2O and gaseous CO_2 according to equation (8) is 889,700 ± 300 international joules per mole at 30° C. and a constant pressure of 1 atm. For small changes in temperature and pressure this value changes, respectively, −93 joules per mole per degree increase in temperature and −6.7 joules per mole per mm increase in pressure.

From the present data the heat of combustion of CO in O_2 to form CO_2 according to equation (13) is 282,925 ± 120 international joules per mole at 30° C. and a constant pressure of 1 atm. For small changes, this value changes, respectively, +7 joules per mole per degree increase in temperature and −3.7 joules per mole per mm increase in pressure.

At 25° C., and a constant pressure of 1 atm., these values in various units [20] are, per mole:

	International joules	Absolute joules	g-cal$_{15}$
CH_4	890, 160 ± 300	890, 520 ± 300	212, 790 ± 70
CO	282, 890 ± 120	283, 000 ± 120	67, 623 ± 30

These values are obtained by using the relations: 1 international joule ~ 1.0004 absolute joules, and 1 g-cal$_{15}$ ~ 4.185 absolute joules.

VII. ACKNOWLEDGMENT

This work is part of the program of thermochemical research which is being carried on at this bureau under the direction of E. W. Washburn, and the author is greatly indebted to him for his deep interest and helpful advice. The assistance of F. A. Smith in developing the flame technic is gratefully acknowledged.

WASHINGTON, October 11, 1930.

[20] See footnote 1, p. 38.

A PORTABLE INSTRUMENT FOR MEASURING AIR PERMEABILITY OF FABRICS

By H. F. Schiefer and A. S. Best

ABSTRACT

A self-contained instrument for measuring the flow of air through fabrics is described. The specimen to be tested is clamped between two orifice rings under a slight tension. Air is drawn through the fabric and through a calibrated orifice meter by a suction fan. The pressure drop across the fabric and across the orifice meter are measured, respectively, by inclined and vertical water gauges. The volume of air passing through the fabric at a given pressure drop is thus obtained. With a set of nine orifices ranging in diameter from 1 to 16 mm the flow of air may be measured for a wide variety of fabrics, ranging from closely woven to loosely knit constructions. Three typical air permeability curves are shown. Typical data for two specimens taken from different portions of the same silk cloth are given and discussed. It is shown that the variation in air permeability because of the nonuniformities in the cloth is greater than the experimental uncertainty.

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I. INTRODUCTION

For certain specific uses of fabrics, the air permeability or rate of air flow through the interstices of a fabric under given conditions is an important property along with the other physical properties and characteristics. In a paper on The Structure and Properties of Parachute Cloth,[1] McNicholas and Hedrick have pointed out the fact that the air permeability of parachute cloth may affect the performance of the parachute. This has since been substantiated by Cleary [2] in a paper on Parachute Cloth. He reports, that a parachute made from cloth whose air permeability is considerably more than that of the standard parachute silk cloth descended at a rate slightly, although not dangerously higher than that of the parachute using the standard cloth. While a parachute made from cloth whose air permeability is considerably less than that of the standard parachute silk cloth descended at a very slow rate, but did not satisfactorily withstand the high opening stresses, especially on delayed opening.

The comfort of under and outergarments depends to some extent on the air permeability. In a recent paper on Determination of

[1] Technical Notes, National Advisory Committee for Aeronautics, No. 335.
[2] Parachute Cloth, The American Silk J.; June, 1930.

Waterproofness,[3] Barr suggests that a determination of waterproofness of fabrics should necessarily and regularly be accompanied by a determination of air permeability. For two waterproofing processes which lead to the same degree of waterproofness in a fabric of given construction, that which leaves the fabric more porous to air would apparently be the more efficient since waterproofness has been attained by reducing the extent to which the yarns are wetted by water rather than mechanical obstruction of the interstices. The more porous sample will probably, though not necessarily, be more permanent in use since the proofing material is better supported. Other uses where the air permeability of fabrics is an important property could be cited.

An apparatus for measuring the air permeability of fabrics accurately, quickly, and conveniently is desirable. Two previous designs of air permeability instruments used in the textile section of the Bureau of Standards have been described by Sale and Hedrick [4] and by McNicholas and Hedrick [5] in previous publications.

In the apparatus described by Sale and Hedrick, the volume of air drawn through a definite area of the fabric at a pressure drop of 1 mm. of water across the fabric was measured by means of a wet gas meter and a stop watch. The drop in pressure across the fabric was from atmospheric to below atmospheric. The air drawn through the fabric was conditioned to 70° F. and 65 per cent relative humidity. The capacity of the apparatus was small so that in connection with the study of parachute cloth by McNicholas and Hedrick another apparatus was constructed to meet the required greater capacity. In this apparatus the volume of air blown through a definite area of the fabric at a definite pressure drop across the fabric was measured by means of a dry gas meter and a stop watch. The drop in pressure across the fabric was from above atmospheric to atmospheric. The flow of air could be measured for pressure drops between 0.02 and 1 inch of water. The air which was blown through the fabric was not conditioned. This may introduce an uncertainty in the results. This apparatus was not well adapted for small rates of flow, because the time interval necessary to determine the rate of flow at one pressure drop was great. It was also difficult to maintain the pressure drop across the fabric constant during this interval.

To overcome the disadvantages of these two instruments a portable air permeability apparatus was designed and constructed. With this apparatus the rate of air flow can be measured accurately and rapidly at any pressure drop across the fabric between 0.01 and 1 inch of water. It is also suitable for testing a wide variety of fabrics, ranging from closely woven to loosely knit constructions.

II. PORTABLE AIR-PERMEABILITY INSTRUMENT

The portable air-permeability instrument was designed by the junior author in 1928. It has been used by members of the textile section in connection with an investigation of the development of superior parachute cloth for the Bureau of Aeronautics, by members of the testing section in determining the rate of air flow through such

[3] Dept. Sci. and Ind. Research, 2d Rpt., Fabrics Coordinating Research Committee; 1930 (London), His Majesty's Stationery Office.
[4] B. S. Tech. Paper, No. 266.
[5] See footnote 1, p. 51.

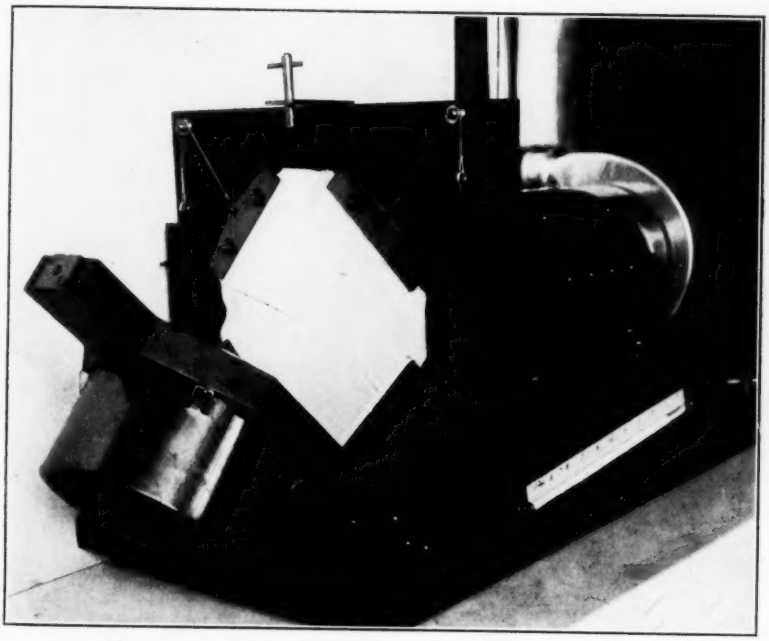

FIGURE 1.—*Air permeability instrument (front view)*

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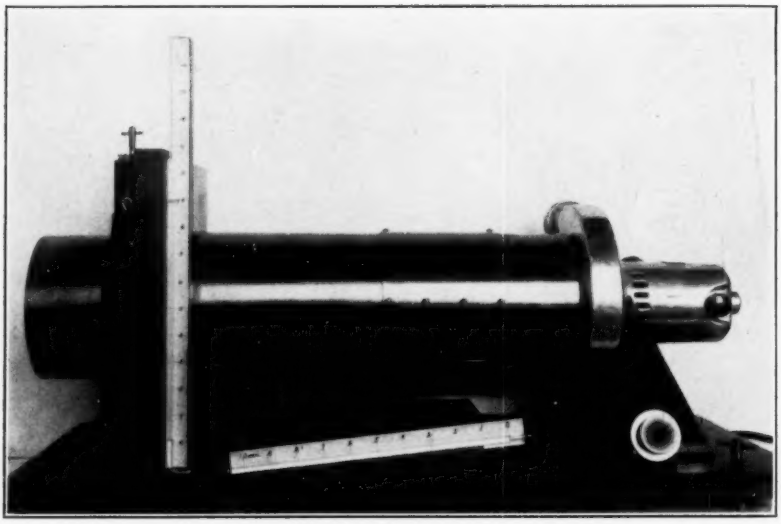

FIGURE 2.—*Air permeability instrument (side view)*

fabrics as are used for winter flying clothing, by Downey[6] in determining the rate of air flow through fabrics for outergarments, and by Hamlin[7] in determining the rate of air flow through fabrics for undergarments.

1. DESCRIPTION

In Figures 1 and 2 are shown two views of the instrument. A schematic diagram is shown in Figure 3. A specimen, 7 inches square, of the fabric to be tested for air permeability is mounted under a slight tension. (Fig. 1.) The hood is then clamped in position (fig. 2), thereby clamping the fabric securely between the two orifice rings (fig. 3). A definite area of the fabric 0.04125 square foot for this apparatus, is thus exposed through which air, conditioned to 70° F. and 65 per cent relative humidity, is drawn by means of a suction fan located at the discharge end. The pressure drop across the fabric is measured by means of an inclined water gauge. The slope of the gauge is 1 to 10. With the apparatus carefully leveled the pressure

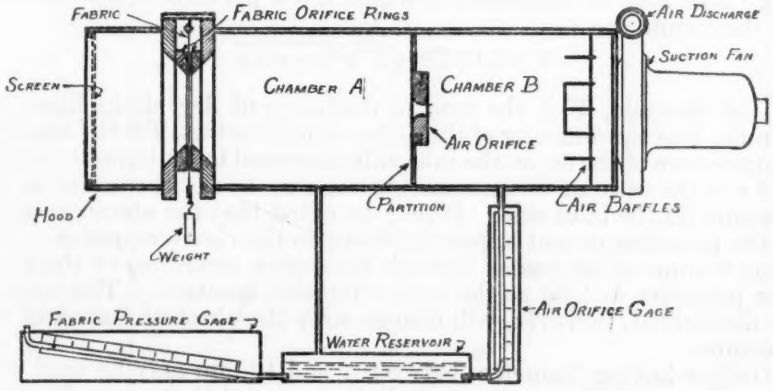

FIGURE 3.—*Air permeability instrument (schematic diagram)*

drop can be measured with an accuracy of five-thousandths of an inch of water. By increasing the slope of this water gauge the air permeability can be measured for a pressure drop greater than 1 inch of water.

The volume of air passing through the fabric is expressed in cubic feet per minute per square foot of fabric at the given pressure drop across the fabric. It is obtained from the pressure drop across a calibrated air orifice. The air orifice is located between chambers *A* and *B*. (Fig. 3.) The pressure drop across it is measured by means of a vertical water gauge with an accuracy of five-hundredths of an inch. The rate of air flow through the fabric at pressure drops up to 1 inch of water may be obtained by increasing the speed of the suction fan. For fabrics of widely different air permeabilities, air orifices of different diameters are used.

The two water gauges are connected to the bottom of a single water reservoir. The top of the reservoir is connected to chamber *A* between the fabric and the air orifice. The upper end of the inclined

[6] Fabrics for Children's Play Suits, Textile World; July 19, 1930.
[7] Research associate for the Associated Knit Underwear Manufacturers of America.

water gauge is open to the air, while the upper end of the vertical water gauge is connected to chamber B on the discharge side of the air orifice. The surface area of the reservoir is large compared to the cross-sectional area of the water gauges so that the water level in the reservoir is practically constant.

2. AIR ORIFICES

The data used in the design of the air orifices was obtained from Bureau of Standards Technologic Paper No. 183, Notes on Small Flow Meter for Air, Especially Orifice Meters, by Edgar Buckingham. The orifices have trumpet-shaped entrances and a straight cylindrical length of one-fourth the diameter. The relations of the thickness, L, and the radius of the profile of the entrance curve, R, to the diameter of the orifice, D, are as follows: $L=1\frac{1}{2}\ D$ and $R=1\frac{1}{4}\ D$. The entrance curve should be tangent to the entrance face of the plate and to the cylindrical portion of the orifice. If the orifices are accurately made and their surfaces very smoothly finished then the rate of air flow may be calculated to within a few per cent of the true rate by the formula

$$V=2.12\ D^2\ \sqrt{T\ (r^{1\frac{6}{7}}-r^{1\frac{2}{7}})}.$$

In this formula, V is the rate of discharge of dry air in liters per minute, D is the diameter of the orifice in millimeters, T is the absolute temperature of the air on the inlet side expressed in centigrade degrees, and r is the ratio of the pressure on the exit side of the orifice to the pressure on the inlet side. It may be noted that the absolute values of the pressures do not appear explicitly in the above equation. The same volume of air passes through the orifice regardless of the absolute pressures as long as the ratio r remains constant. The mass of air discharged, however, will change with the absolute values of the pressures.

Orifices having diameters between 1 and 16 mm may be used with the air permeability apparatus. It is suggested that a set of orifices be used having diameters 1, 1.4, 2, 3, 4, 6, 8, 11, and 16 mm, respectively. Each orifice will then have approximately twice the capacity of the next smaller one. With such a set of orifices the rate of air flow which can be measured ranges approximately from 1 to 700 cubic feet per minute per square foot of fabric. If one wishes to measure smaller or larger rates than the above, then a larger or smaller area of the fabric should be exposed through which the air is drawn.

The rates of air flow through each of the nine orifices were determined at three pressure drops by the gas-measuring instruments section of the bureau. From these data three discharge coefficients were computed for each orifice. The discharge coefficient is equal to the ratio of the actual flow to the theoretical flow. The average of the three discharge coefficients computed for each orifice was used in computing a calibration table for each orifice. In each table the volume of air in cubic feet passing through 1 square foot of fabric per minute may be read directly for every tenth inch of water up to 15 inches of water pressure drop across the orifice.

The discharge coefficients varied with the pressure drop across the orifice. However, the variations were not regular. Therefore, it seemed advisable to take the average of the three discharge coefficients for an orifice rather than to determine the discharge coefficients

as a function of the pressure drop. The uncertainty in the discharge values was not greater than ±2 per cent, and for the recommended range of pressure drops across an orifice, namely, 2 to 15 inches of water, probably not greater than ±1 per cent. The calibration of the orifices was carried out at a temperature of 15.5° C., the theoretical discharge was computed for a temperature of 18° C. and the apparatus was used at an average temperature of 21° C. At 20° C.

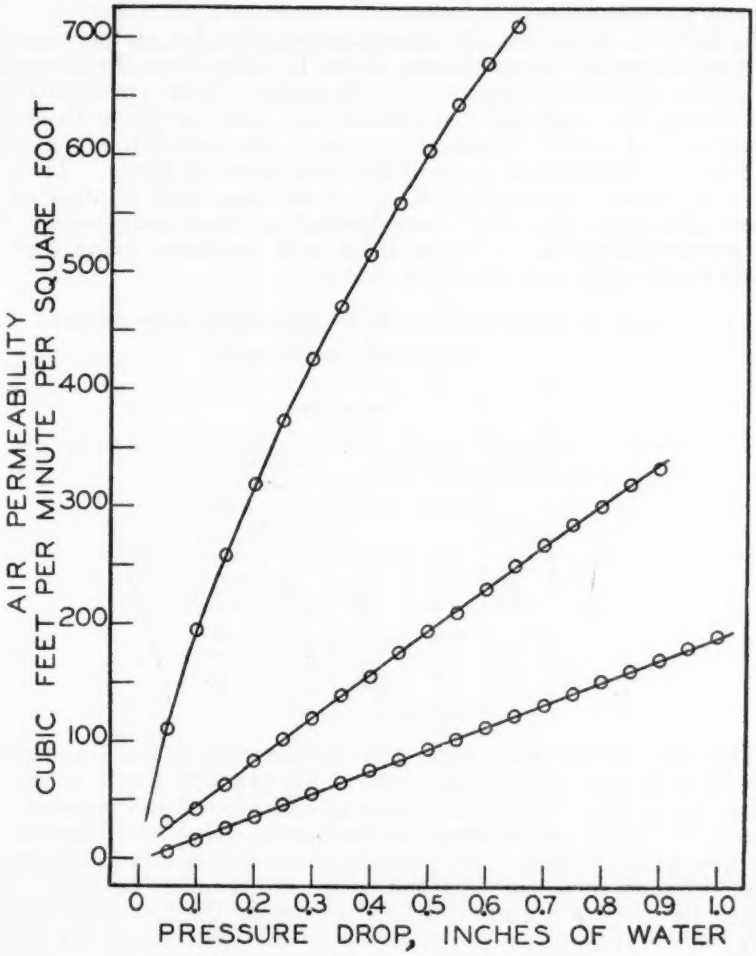

FIGURE 4.—*Typical air permeability curves*

a change of 1° C. changes the value of V by a trifle more than one-eighth of 1 per cent. Since the probable uncertainty in the discharge is ±1 per cent and may be ±2 per cent no correction was applied in the calibration table for the variation in temperature.

III. RESULTS OF TYPICAL TESTS

In Figure 4 are shown three typical air permeability curves furnished by Hamlin. The volume of air in cubic feet passed through

1 square foot of fabric per minute was determined for every five-hundredths of an inch of water pressure drop across the fabric. The rate of air flow is not necessarily proportional to the pressure drop. However, in comparing one fabric with another it will usually suffice to compare the rates of air flow at one pressure drop. For parachute cloth the rate of air flow is usually specified at a pressure drop of one-half inch of water. This may be a convenient pressure drop at which to make all comparisons. It corresponds to a pressure of 2.6 pounds per square foot of fabric.

In Table 1 are given the experimental data for air permeability determinations of two specimens, A and B, taken from the same piece of a well-constructed commercial silk cloth. These specimens were so selected that they did not contain any warp or filling threads in common, and would, therefore, represent the variation which might be expected in different parts of the same piece of goods. The data given in Table 1 are typical of tests made on a large number of different fabrics and the conclusions drawn from them are general. The air permeability was determined for each specimen using first the 6-mm orifice and then the 8-mm orifice.

TABLE 1.—*Typical test data for air permeability determination*

[Pressure drop in inches of water]

Across fabric	Across orifice			
	Specimen A		Specimen B	
	6 mm	8 mm	6 mm	8 mm
0.05	0.10	0.05	0.17	0.08
.10	.48	.16	.63	.24
.20	1.55	.50	1.90	.70
.30	3.20	.95	3.72	1.25
.40	5.05	1.50	5.95	1.90
.50	7.35	2.18	8.50	2.73
.60	9.90	2.90	11.30	3.60
.70	12.75	3.65	14.30	4.50

The data of this table show that in the case of the 6-mm orifice the air flow can only be determined for pressure drops across the fabric up to about 0.7 inch of water at which point the pressure drop across the orifice approaches the maximum value of 15 inches. If the flow of air is desired for pressure drops across this fabric greater than 0.7 inch of water then the 8-mm orifice must be used. This orifice, however, is not suitable for determining the flow of air through this fabric for pressure drops across it less than about 0.5 inch of water, because then the pressure drop across the orifice becomes less than 2 inches and uncertainties are likely to be introduced. For pressure drops across an orifice less than 2 inches of water, the discharge coefficient may be uncertain by ± 2 per cent. Also the pressure drop across the orifice and across the fabric may be uncertain by ± 2 per cent or more if they are equal to or less than 2 and 0.2 inches of water, respectively. Therefore, the flow of air across a fabric may be uncertain by several per cent depending mainly upon the size of the orifice chosen.

This is brought out more clearly in Table 2. The per cent variation for pressure drops across this fabric greater than 0.2 inch of water are small. They are large, however, for pressure drops equal to or less than 0.2 inch of water because of the reasons mentioned above. If the flow of air is desired at these low pressure drops across this fabric, then a smaller orifice should be used so that the pressure drop across the orifice will be greater than 2 inches of water.

TABLE 2.—*Duplication of results by two different orifices*

[Flow of air in cubic feet per minute per square foot of fabric]

Pressure drop across fabric	Speciman A			Speciman B		
	Orifice		Variation	Orifice		Variation
	6 mm	8 mm		6 mm	8 mm	
			Per cent			*Per cent*
0.05	8.4	5.5	40.7	11.0	8.8	22.2
.10	18.9	17.0	10.6	21.4	23.5	9.3
.20	34.0	34.9	2.7	37.6	41.0	8.7
.30	48.5	48.5	0.0	52.2	55.2	5.6
.40	61.2	60.4	1.3	66.7	68.0	1.9
.50	73.9	72.6	1.7	79.3	80.8	1.9
.60	85.2	83.9	1.5	90.4	92.9	2.7
.70	95.8	93.6	2.2	101.5	104.0	2.4

TABLE 3.—*Duplication of results on two different test specimens*

[Flow of air in cubic feet per minute per square foot of fabric]

Pressure drop across fabric	6 mm orifice			8 mm orifice		
	Specimen		Variation	Specimen		Variation
	A	B		A	B	
			Per cent			*Per cent*
0.05	8.4	11.0	27	5.5	8.8	46
.10	18.9	21.4	14	17.0	23.5	34
.20	34.0	37.6	10	34.9	41.0	16
.30	48.5	52.2	7	48.5	55.2	13
.40	61.2	66.7	9	60.4	68.0	12
.50	73.9	79.3	8	72.6	80.8	11
.60	85.2	90.4	6	83.9	92.9	10
.70	95.8	101.5	6	93.6	104.0	11

The data in Table 3 show that the per cent variation, while again greater at the lower pressure drops across the fabric than at the higher, is larger than the experimental uncertainty. The larger per cent variation must be attributed to an actual variation in the fabric with respect to air permeability. The 6-mm orifice shows approximately 6 per cent variation in the two specimens while the 8-mm orifice shows approximately 11 per cent variation. The greater variation shown by the 8-mm orifice is undoubtedly due to the greater experimental uncertainties at the smaller pressure drops across the 8-mm orifice.

IV. SUMMARY

The portable air permeability apparatus described in this paper can be used to determine the rate of air flow through a great variety of fabrics at pressure drops up to 1 inch of water. By a proper choice of air orifices the uncertainty for an air permeability determination will be less than ±2 per cent. This is less than the variation observed between specimens taken from different portions of the same fabric.

Details for the construction of the portabe air permeability apparatus described in this paper may be obtained from the textile section of the Bureau of Standards.

PRISM SIZE AND ORIENTATION IN MINIMUM-DEVIATION REFRACTOMETRY

By L. W. Tilton

ABSTRACT

An investigation of the optical error in the pointing of telescopes, and of variations therein with width of objective aperture, indicates that the effect of marginal aberration is often sufficiently deleterious to seriously impair the advantages which should result from the use of the larger apertures. The utility of larger prisms for more accurate index measurement is, therefore, subject to question. The experienced ratios of the probable error in pointing to the limit of angular resolution are, moreover, smaller than was expected for the narrower effective widths of telescope apertures and frequently they do not exceed 1/30. For sixth decimal place determinations of refractive index by minimum-deviation measurements when using a 60° prism, it is shown that a suitable and sufficient length of prism surface is approximately 2 cm, a constant value for all transparent media.

The systematic errors in measured index which result from improper orientation of a prism for minimum deviation are discussed. It is found that the residuals in prism azimuth as determined by simple hand and eye adjustment have an approximately normal distribution, and that their average values do not vary greatly with wave length. The requisite precision in azimuthal orientation is quantitatively established and the corresponding tolerances for prisms having various indices and refracting angles are expressed by contours. These curves may be used for evaluating prism-orientation corrections to index measurements. It is concluded that large telescope apertures and special procedures for securing accuracy in prism orientation are unnecessary in minimum-deviation measurements leading to an approximate precision of P. E. $= \pm 1 \times 10^{-6}$ in the computed index of refraction.

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I. INTRODUCTION

In a previous paper[1] on certain aspects of prism refractometry it was assumed that the errors of telescope pointings do not constitute a serious problem even when seeking to attain a precision extending to the sixth decimal place in index of refraction. In the design of spectrometers for high accuracy in index measurement, however, the desirability of increasing the pointing accuracy by providing rather wide apertures in the telescopic system is quite generally implied and sometimes it is definitely stated that the greater widths are necessary for obtaining sufficient precision in angular measurements. Since effective aperture is dependent on the length or horizontal extent of the polished vertical surface of the prism, it therefore becomes of considerable importance to determine the requisite dimensions of a prism for index measurements of a stipulated accuracy by means of a given number of minimum-deviation observations. In the investigation of prism size, and also in the related problem of establishing the necessary precision in the azimuthal orientation of a prism, the most important factors to be considered are the accuracy with which telescopes may be pointed and the degree of homogeneity of the refracting media.

The first of these factors, the metrological power of telescopes, has not received adequate attention in spectometry, perhaps because it has usually been second in importance to the question of homogeneity. It appears, however, that several types of optical glass may be improved in the degree of their index uniformity [2] by a modified heat-treatment procedure, a carefully executed isothermic annealing,[3] and consequently it now seems appropriate to consider the questions of prism size and orientation from the standpoint of the metrological accuracy of telescope pointings.

Although the accuracy and precision which are discussed in this paper are based on optical considerations only, it should be noticed that no general assumption concerning an equivalent excellence in the mechanical design of a spectrometer is directly implied. For example, the maximum prism size which it is proposed to establish is not a value necessarily required for optimum work on a given instrument. It should be viewed simply as an upper limiting size which need not be exceeded when seeking a specified accuracy of index measurement. Moreover, the required systematic correction to index measurements which involve ordinary procedures in prism orientation is, for a given observer, approximately independent of errors other than those which are optical in nature and affect telescope pointing.

The symbols used are explained in the text, but for convenience of reference the definitions of the various characters are summarized here as follows:

$A \equiv$ the refracting angle of a prism;
$D \equiv$ the angle of minimum deviation produced by a prism;
$\Delta D \equiv$ a small departure from minimum deviation which is caused by an error in prism orientation;
$i \equiv$ the angle which an incident ray makes with the normal to the face of a prism;

---

[1] L. W. Tilton, B. S. Jour. Research, **2** (RP64), p. 923; 1929.
[2] L. W. Tilton, Variations in the Optical Density of Glass, Meeting, Philosophical Soc., Washington, May, 1929. Abstract in J. Wash. Acad. Sci., **20**, pp. 12–13; 1930.
[3] L. W. Tilton, A. N. Finn, and A. Q. Tool, B. S. Sci. Papers (No. 572), **23**, pp. 719–736; 1927–28. See also J. Am. Ceram. Soc., **11**, pp. 292–295; 1928.

$\Delta i \equiv$ a small error in the orientation of a prism for minimum deviation;

$K \equiv$ the ratio between limiting precision of angular measurement and limit of angular resolution;

$L \equiv$ the length or horizontal dimension of a prism face or surface;

$L_D \equiv$ the maximum prism surface length which is required for (double) minimum-deviation index measurements having an accuracy of $\pm 1 \times 10^{-6}$;

$\lambda \equiv$ wave length;

$m \equiv$ the limiting precision of angular (telescopic) measurement expressed in terms of (the absolute value of) the probable error of a single pointing;

$m' \equiv$ the probable error of the mean of N observations of an elemental angular magnitude in minimum-deviation refractometry;

$N \equiv$ the number of complete determinations of an angular magnitude;

$N_A \equiv$ the number of measurements of the refractive angle of a prism from the mean of which there may be computed an index having a probable error of $\pm 1 \times 10^{-6}$;

$N_D \equiv$ the number of determinations of (double) minimum deviation from the mean of which there may be computed an index having a probable error of $\pm 1 \times 10^{-6}$;

$n \equiv$ the relative index of refraction of a medium;

$r \equiv$ the limit of angular resolution with a telescope;

$T_A \equiv$ the tolerance, in measuring refracting angle, which corresponds to an error of $\pm 1 \times 10^{-6}$ in the measurement of refractive index;

$T_{2D} \equiv$ the tolerance, in measuring double minimum deviation, which corresponds to an error of $\pm 1 \times 10^{-6}$ in the measurement of refractive index;

$T'_{\Delta i} \equiv$ the tolerance in each prism orientation which corresponds to an error of $+1 \times 10^{-6}$ in the index computed from a single observation of double deviation; and

$T_{P.E.i} \equiv$ the tolerance in precision of a series of prism orientations which corresponds to an error of $+1 \times 10^{-6}$ in the index computed from the average observed minimum deviation.

II. ON THE PRECISION OF TELESCOPE POINTINGS

Both Michelson [4] and Wadsworth [5] have discussed the limiting precision of angular measurement or metrological limit, m, which may be attained with a telescope, and have related it to the limit of angular resolution, r, in the form of an equation

$$m = Kr \tag{1}$$

where K is a factor to which Michelson assigns a value of 1/4 or 1/5 while Wadsworth cites experimental evidence showing that certain errors in telescope pointings correspond to a value as small as 1/15 for this parameter.

[4] A. A. Michelson, Am. J. Sci., **39**, p. 115; 1890. Nature, **49**, pp. 56–60; 1893–94.
[5] F. L. O. Wadsworth, Phil. Mag., **44**, pp. 83-97; 1897. Astrophys. J., **16**, pp. 267–270; 1902.

It is well known that the value of K is greatly influenced by certain conditions of measurement, particularly by the degree of magnification which is used; also such matters as contrast and intensity of illumination are sometimes mentioned as important. The effect of spherical aberration in causing variations [6] in K is another matter to be considered. This subject first engaged the writer's attention because of certain favorable results which were obtained in measuring angles and indices of refraction of small prisms. Later, when using small apertures under relatively unfavorable conditions of illumination, it was found that the probable errors of a single micrometric pointing corresponded to values of K as small as 1/40, whereas with the full apertures of the same lens systems the values ranged from 1/11 to 1/17. Incidentally, these last-named values of K are in good agreement with the above-mentioned limits which were named by Wadsworth and which, presumably, were also obtained at full apertures.

1. RATIO OF METROLOGICAL AND RESOLUTION LIMITS

The spectrometer objectives which were used for taking the data of Figure 1 have clear apertures of 47 mm and focal lengths of 40 cm. They give good optical definition and have "full theoretical" resolving power, even at full apertures. The eyepiece has a focal length of 11 mm so that the total magnification of the telescope is approximately 37; a value which has hitherto been considered sufficiently high for a telescope of this size. In most instances a vertical spider hair was mounted in the plane of a wide collimator slit and 60° crossed spider hairs were used as the movable reference marks in the focal plane of the telescope. The precision of pointings made with a narrow bright-line slit as the object does not, however, differ very significantly from that obtained when using the spider hair object, as is shown by a comparison of curves A and B of Figure 1.

In view of the possible effects of the intensity of illumination,[7] curve C was obtained for an electric light source which was very bright as compared with the monochromatic radiation ($\lambda = 5461$A) used for the other curves. It seemed, therefore, that variations in intensity were not of importance [8] in this case but the various apertures were, nevertheless, made of equal area (see fig. 1) so that equal intensities were employed when varying the resolving power by these apertures of different widths.

The effect of eyestrain and fatigue of the observer in observations of this character is thought to be so important that but little significance should be attached to the differences in absolute value as depicted by the different levels of these three curves of Figure 1. Moreover, it should be mentioned that the curves are drawn directly through the plotted points, not because it is thought that the slopes are determined with a corresponding accuracy, but merely to avoid the personal element which would affect a smoothing process.

[6] Since K is merely a ratio between certain angular limits, its variations with aperture do not in themselves give any information concerning variations in the absolute values of the pointing errors. It may, however, be assumed that the degree of its constancy is an indication of the type of aberration correction which has been achieved in an objective.

[7] A. Pelzer, Zeitschr. für Instrumentenkunde, **46**, p. 374; 1926.

[8] The plotted points for curve C depend on only 6 sets of 10 observations each as compared with 8 and 10 similar sets for the other curves.

2. EFFECTS OF ABERRATION AND MAGNIFICATION

The curves of Figure 1 indicate that, with the objectives used, an appreciable increase in pointing accuracy can not be gained by an increase in prism size. Although the use of higher eyepiece magnification was found to be advantageous at the medium and larger apertures, values of K more favorable than 1/17 were not reached for the full objective width. The data thus seem to call in question the validity of the assumption that metrological power is directly related to resolution. The only explanations herein offered, however, are (1) that the values of K which are optically attainable in angular measure-

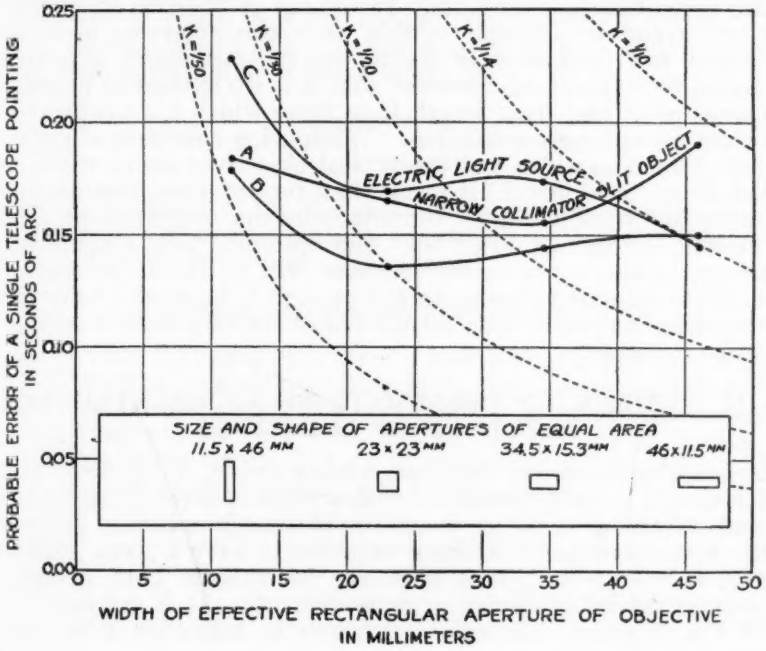

FIGURE 1.—*Nonconstancy in the ratio, K, of probable error in telescope pointing to Dawes' limit of resolution*

These data were obtained with spectrometer objectives having focal lengths of 40 cm. The focal length of the eyepiece was 11 mm. With the exceptions noted, monochromatic light (λ=5,461Å) was employed and the object sighted was a vertical spider hair in the collimator slit. Objective apertures of equal area were used, as shown in the inset.

ments with a telescope are much more favorable than have hitherto been explicitly reported in the literature, and (2) that aberration of the outer zones of the lenses plays a conspicuous part in the metrological performance of telescope objectives.[9]

In fact, a confirmation of these views seems to be contained in the data which Noetzli [10] published when determining the variation of pointing accuracy with magnification. By reducing his mean square

[9] In this connection it is of interest to refer to the experiments reported by Guild (Trans. Opt. Soc., **31**, pp. 1–14; 1929–30) on the precision of optical settings made by means of the unaided eye. The fact that his results are approximately independent of pupillary aperture may, perhaps, also be due to a masking effect of increased aberration when using the wider apertures.

[10] A. Noetzli, Zeitschr. für Instrumentenkunde, **35**, pp. 65–73; 1915.

errors to probable errors and using his experimentally determined limits of resolution (which seem unaccountably small) the values of K may be computed and they are found to range from 1/30 to 1/60 for the reduced apertures which were used in pointings with the 41 cm objective, but they are almost as large as 1/20 for the full apertures of the 51 cm focal length objective.

Moreover, further investigations in progress in this laboratory indicate that 1/25 or 1/30 are values of K which are approximately constant and, from an optical standpoint, are easily attainable when using typical [11] spectrometer objectives of 40 or 50 cm focal length for measurements on prisms of any reasonable size provided they do not utilize more than approximately two-thirds of the clear apertures of the lens systems. In some of this work two observers have been employed and their average results are in satisfactory agreement. It should be emphasized, however, that it is advantageous to employ eyepieces of shorter focal length than those which are considered as sufficient for optimum resolution. When using apertures of approximately 2.5 cm in width and the typical objectives above mentioned (40 or 50 cm focal length) it seems that, for obtaining the maximum accuracy in optical pointings, the total telescope magnification should be at least as high as 40 or 50. The optimum total magnification does not, however, necessarily increase with width of aperture. In fact, these optimum values appear, in general, to be greater when using intermediate apertures than for the full or for very narrow widths of effective openings.

III. NUMBER OF OBSERVATIONS AS RELATED TO PRECISION OF POINTINGS

In order to determine the appropriate number, N, of observations which should be used in making, with a prism of given surface length, L, and refracting angle, A, a number of measurements of refractive index, n, the average of which is expected to have a given precision, say P. E. $= \pm 1 \times 10^{-6}$, it is necessary to consider both refractive-angle and minimum-deviation measurements. It is convenient to recall [12] appropriate elemental tolerances in refractive-index goniometry, such as

$$T_A = \pm 0.413 \frac{\sin^2 A/2}{\sin D/2} \text{ seconds} \tag{2}$$

for measurements on the refracting angle, and

$$T_{2D} = \pm 0.825 \frac{\tan\left(\frac{A+D}{2}\right)}{n} \text{ seconds} \tag{3}$$

[11] The adjective "typical" is used to designate objectives which have an approximately constant value of K, at least over two-thirds or three-fourths of their apertures. Such lens systems permit a real increase in pointing accuracy as effective width of aperture is increased, whereas it seems possible that objectives of special or unusual design may favor the use of small apertures at the expense of the accuracy which can be attained with the larger objective widths. The 40-cm objectives, used in the observations represented in Figure 1, appear to be examples of the special class, and it is suggested that the 41-cm objective used by Noetzli may also be of the same character. The metrological performance of such lens systems may be summarized as unusually good at small apertures and somewhat worse than normal at full apertures. The defective performance at the larger apertures may be aggravated by the use of insufficient eyepiece magnification. This is known to be the case in Figure 1 because the total magnification of 37 was afterward found inadequate except at the 11.5-mm aperture. Optical systems having this special character of correction are especially desirable in spectrometry for work on small prisms, but for larger prisms they may decrease the actual precision of pointings.

[12] See p. 921 of paper cited in footnote 1.

for observations of double deviation. These tolerances correspond to an accuracy of $\pm 1 \times 10^{-6}$ in index measurements. Moreover, it will be assumed that the telescope system is sufficiently free from aberration to permit a resolution increasing at the theoretical rate with the widths of the rectangular apertures actually employed; that is, a limit of resolution expressible as

$$r = \frac{\lambda}{L \cos i} \tag{4}$$

where i is the angle which the incident rays make with the normal to the face of the prism. Then from equations (1) and (4) the probable error, arising solely from the optical pointings made during N complete determinations of an angular magnitude, such as that of double minimum deviation or of prism angle, is

$$m' = \pm \frac{206 \times 10^3 K \lambda \sqrt{2}}{L \cos i \sqrt{N}} \text{ seconds} \tag{5}$$

where $\sqrt{2}$ appears in the numerator because both positive and negative errors in telescope pointings are equally probable at the right and at the left-hand observational positions.

1. REFRACTIVE-ANGLE MEASUREMENTS

It is found that prism size is not a troublesome factor in prism-angle measurements because repetition is in this case quite useful in the reduction of the errors. It is desirable, however, to express the relationship which should exist between the number of observations, N, and the prism length, L, for a requisite precision of refractive angle measurement in minimum-deviation goniometry.

The elemental tolerance equation (2) is applicable in this case, and equation (5) applies to the measurement of prism angles by the method of autocollimation provided the appropriate value of 0° is assigned to the angle i. By imposing suitable tolerance conditions one may equate the right-hand members of equations (2) and (5) and obtain

$$N_A = \left(\frac{7 \times 10^5 \, \mathrm{K} \, \lambda \sin \mathrm{D}/2}{L \sin^2 A/2} \right)^2 \tag{6}$$

which is a general statement of the appropriate relationship between N_A and L. The subscript, A, is used to denote that this particular value of N is determined by the precision required in the refractive-angle measurements. The presence of D in equation (6) shows that the index, as well as the angle of the prism, is involved in determining, from the standpoint of angle-measuring accuracy, the necessary number of observations for use in minimum-deviation refractometry. Equation (6) is optically consistent with probable errors in the mean value of the refractive angle which, in turn, are equivalent to $\pm 1 \times 10^{-6}$ in the computed index of refraction. If it be assumed that the magnification, the contrast conditions in the image, and the aberration of the prism are consistent with a normal value of K, then the proper N_A and L relationship for use in sixth decimal place refractive-index measurements by the minimum-deviation method is numerically determinable. Considering 0.55μ as the effective wave length of

white light (which is used in prism-angle measurements), and using for K the value 1/25 which, according to the author's experience (see Section II), is fairly conservative, equation (6) becomes

$$N_A=\left(\frac{6.2 \sin D/2}{L}\right)^2 \tag{7}$$

for 60° prisms, if L is expressed in centimeters. When using indices of 1.4, 1.6, and 1.8, respectively, it will, therefore, be found that prism surface lengths (or horizontal dimensions of the polished vertical faces) of 1.5, 2.4, and 3.5 cm are ample, even if but one measurement of prism angle is to be made.

2. MINIMUM-DEVIATION MEASUREMENTS

The proper relationship between number of observations, prism size, and error in minimum-deviation measurement is dependent on the use or nonuse of special procedures for prism orientation in azimuth and these two cases should be considered separately. The general case in which no special procedures are used is of more importance than the special case because the usefulness of repeated observations is rigorously limited and thus more severe requirements are imposed on prism size. Since, however, the general case involves a consideration of the systematic errors in prism orientation (see Section IV), its discussion is deferred and appears in Section V.

In the special case, correct prism azimuth being assured, the only optical errors involved are the accidental errors of the two telescope pointings. By imposing suitable tolerance conditions one may equate the right-hand members of equations (3) and (5) and obtain a result which may be written as

$$N_D=\left(\frac{35\times10^4 K\lambda}{L \sin A/2}\right)^2 \tag{8}$$

for the particular conditions which exist at the minimum-deviation position of a prism. The subscript, D, is used to denote that this value of N is determined by considerations of the requisite precision in deviation measurements. Equation (8) expresses a relationship between N and L which is optically consistent with probable errors in the mean angle of double deviation which, in turn, are equivalent to $\pm1\times10^{-6}$ in the computed index of refraction. Obviously there is under these conditions no severe requirement concerning prism size because of the important effect of a few repetitions in measurement. Considering, however, only the unfavorable case of long wave length radiation ($\lambda=0.7\mu$), and again using for K the value 1/25, equation (8) becomes approximately

$$N_D=\left(\frac{4}{L^2}\right) \tag{9}$$

for 60° prisms, provided L is expressed in centimeters. Consequently, when making but a single observation of double deviation, it is found that a 2-cm length of prism surface is all that is required. It should be noticed that this result is independent of the value of the deviation.

IV. PRISM ORIENTATION IN AZIMUTH AND ITS RELATION TO DEPARTURES FROM MINIMUM DEVIATION

The precise orientation of a prism for minimum deviation is a rather troublesome procedure, and the matter is sometimes referred to as a disadvantage of this method of index measurement. The difficulty arises because the errors in orientation, irrespective of their sign, give rise to corresponding departures from minimum deviation which are always positive. Furthermore, upon repeating the observations, the average of all of these errors in the deviation tends toward some definite value which is not zero.

In order to overcome this difficulty Hastings [13] computed the proper prism orientations and set the table accordingly after determining one reference position experimentally. Macé de Lépinay [14] noted two slightly different orientations which produced identical total deviation and then used the mean azimuth of these two orientations. Schönrock [15] computed the correct angles of incidence from preliminary data and then used reflections from the prism surfaces in making precise orientations of the prism.

Most of these special procedures require, or are facilitated by, a circle for measuring the azimuth of the prism table; a feature which is often lacking. When required to make this prism adjustment without the measurement of table orientation, one may follow Carvallo [16] and Gifford,[17] each of whom utilized reflections from the polished third side of a prism, the former even making corrections for nonisoscelism of the prism and for refocusing. This artifice, however, will not always work when the prism is placed on the table in such manner as to permit the symmetrical use of all apertures. For example, the intensity of the reflected image may be sufficiently great to interfere with precise pointings on the refracted image; or, on the other hand, for large prisms, the reflected image may be entirely absent because the necessary rays do not enter the objective. Consequently, it is desirable to quantitatively investigate the magnitude of the systematic errors which occur in practice and also to determine the requisite precision in prism table orientation in order to determine the exact circumstances in which special methods of prism orientation are necessary.

1. EXPERIENCED PRECISION OF SIMPLE ORIENTATION

Considering, then, the attainable degree of precision in the orientation of a prism, by simple hand adjustment and by observation of the deviated image, it appeared, as stated by Wadsworth,[18] quite possible to attain such precision that the error in minimum deviation does not exceed the approximate limiting metrological accuracy of the effective telescope aperture. This limit, as stated in Section II, 2, is more favorable than has hitherto been recognized; and, in the experience of two observers in this laboratory, is almost always less than ± 0.2 seconds as measured by the probable error of a single pointing.

[13] C. S. Hastings, Am. J. Sci., **15**, p. 272; 1878.
[14] J. Macé de Lépinay, Annales de Chimie et de Physique (7), **5**, p. 227; 1895.
[15] O. Schönrock, Zeitschr. für Instrumentenkunde, **40**, p. 95; 1920.
[16] E. Carvallo, Annales de l'Ecole Normale Superieure (3), **7**, supplement, pp. 75 and 93; 1890.
[17] J. W. Gifford, Proc. Royal Soc., London, **70**, p. 330; 1902.
[18] F. L. O. Wadsworth, Astrophys. J., **16**, p. 269; 1902; **17**, p. 11; 1903.

It thus seemed improbable,[19] in the practice of prism refractometry, that the errors resulting from prism-orientation inaccuracies would exceed $+1\times10^{-6}$ in index. In fact, Schönrock [20] reports for certain data an average error of $+0.25''$ in D, due to prism orientation in the usual way, that is, a value which is equivalent to less than $+1\times10^{-6}$ in refractive index.

An extended series of prism-orientation error determinations has been made by the writer in order to investigate the above-expressed views. These experiments were made on a prism of 45° refracting angle with an index of 1.52 for sodium light and included the use of various wave lengths and several different aperture widths of the

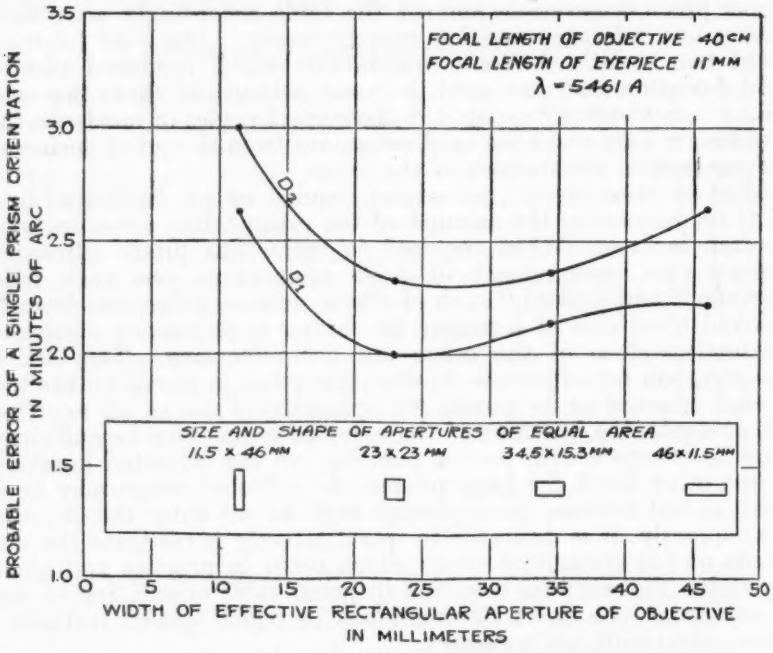

FIGURE 2.—*Experimental precision of prism orientation for various apertures*

The data for these curves were taken under conditions identical with those which were employed when obtaining curve B of Figure 1. The observations for curve D_2 were taken somewhat more rapidly than those for curve D_1 and also with greater friction of the prism-table axis. Each plotted point depends on 8 sets of observations having 10 values in each. The prism has a refractive angle of 45° and an index of 1.52 for sodium light.

telescope objective. A plane parallel plate was mounted on the prism table, approximately normal to the rays emerging from the prism. An autocollimating device and a scale in the focal plane of the (stationary) telescope permitted rapid and accurate readings which corresponded to the several azimuths in which the prism was successively adjusted.

(a) VARIATION WITH APERTURE

The apertures used in these orientation experiments are the ones used in the pointing error investigation which is discussed in Section II. Some results of this work are exhibited in Figure 2 which

[19] See figure 2, p. 922 of paper cited in footnote 1.

[20] See footnote 15, p. 67.

shows the probable error in orientation, *P. E. i*, as a function of objective aperture. The observations for curve D_1 of this figure and for curve B of Figure 1 were made alternately in order to secure strictly comparable working conditions, including such factors as eye-strain and fatigue of the observer. A marked similarity in the slopes of these curves (B and D_1) suggests an intimate connection between prism orientation and pointing precision. This relationship is investigated and quantitatively evaluated in Section V, 1. Some preliminary data, taken rapidly and with an unnecessarily large amount of friction of the prism-table axis, yielded somewhat less precision and are represented by curve D_2.

(b) VARIATION WITH WAVE LENGTH

A knowledge of the manner in which orientation error varies with wave length is necessary in order to reach a decision concerning the

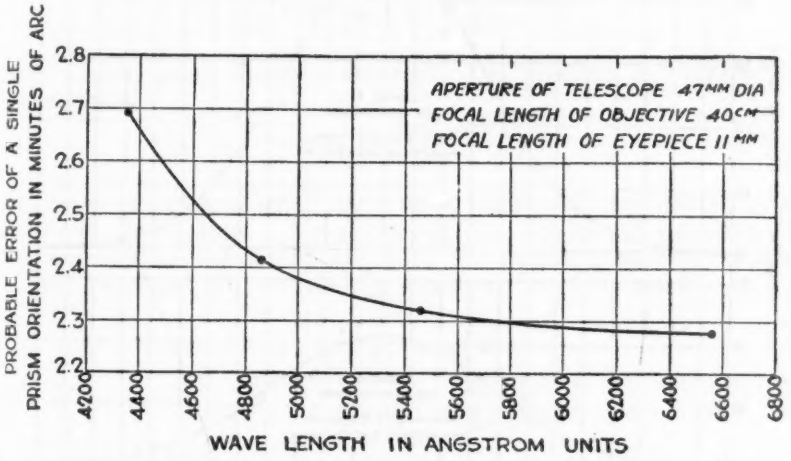

FIGURE 3.—*Experimental precision of prism orientation for various wave lengths*

The advantage of increased metrological power which should result from the use of shorter wave lengths is more than balanced by the deleterious influences of aberration, low visibility, and chromatic parallax.

usefulness of employing special procedures for obtaining accurate orientation. The curve of Figure 3 shows some values of *P. E. i* which were obtained with the previously mentioned 45° prism of 1.52 index of refraction. For each of the 4 wave lengths used these data result from 8 sets consisting of 10 observations each. The increased error corresponding to the use of shorter wave lengths is contrary to expectations. In agreement with this result, however, the writer has also found that errors in micrometric telescope pointing are larger when using radiation of the higher frequencies. It is suggested that relatively greater aberration and lower visibility, together with certain difficulties due to chromatic parallax,[21] may be somewhat more than sufficient to offset the advantages of increased resolution resulting from the shorter wave lengths.

[21] J. Guild, Proc. Phys. Soc., London, **29**, pp. 311–337; 1916–17; or Nat. Phys. Lab., Collected Researches, **14**, pp. 251–270; 1920.

(c) NORMALITY IN DISTRIBUTION OF RESIDUALS

The probable errors shown in Figures 2 and 3 were computed from the average residuals by Peters' formula and thus involve the assumption that the errors in orientation have a normal distribution. Moreover, in part 2 of this section it is found that if such an error distribution exists, the evaluation of a tolerance in the precision of prism orientation is facilitated. Consequently, in lieu of an assumption concerning this distribution, there is presented in Figure 4 some experimental data on the character of the error curve which is obtained when making prism orientations by the ordinary methods.

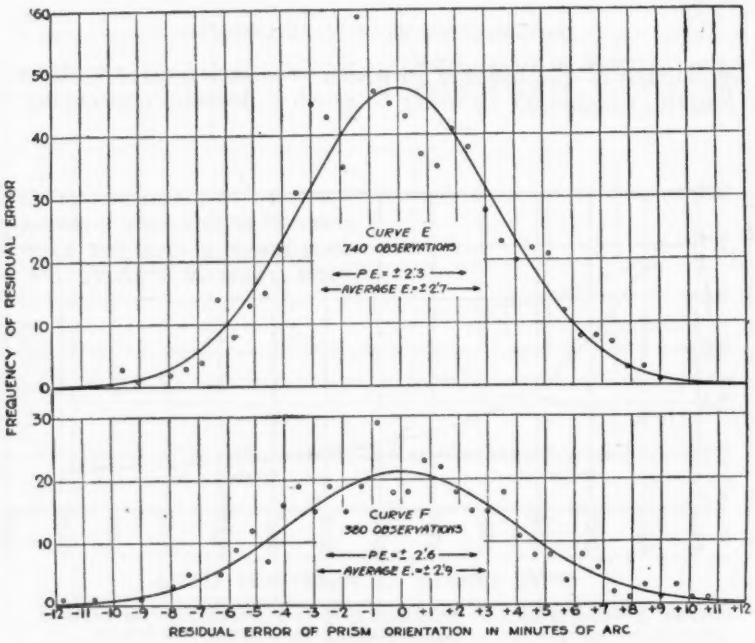

FIGURE 4.—*Normality in distribution of prism orientation residuals*

The plotted points show the number of residuals which were experienced upon grouping the data to the nearest half turn of a micrometer screw for which one turn represents 1.09 minutes of arc. Thus each group extends over an interval of 0.54 of a minute in azimuth. The curves show the theoretical distribution of errors according to the probability equation. The probable errors, as originally obtained by determining the widths of the 50 per cent zones for the individual residuals agree satisfactorily with values computed from the second moments of the grouped data.

A total of 1,120 observations was available for use in this test of the normality in the distribution of the errors in prism orientation. Four different wave lengths had been used and five sizes of aperture were represented. Using the method of grouping, these data were first treated as one composite whole and afterwards separated into the two main divisions, one of a higher and the other of a lower precision, which give rise to the curves *E* and *F* of Figure 4. On both of these curves, and also for the composite curve which is not reproduced, the total number of negative residuals is slightly in excess of that for the positive residuals and the residual group in which the largest number of residuals is found is also of negative sign. Aside

from this slight and negligible [22] skewness, which indicates the writer's tendency to favor small excess clockwise orientations, and also to obtain moderately large positive residuals, the agreement of the experimentally determined points with the normal curves is very satisfactory.[23]

2. TOLERANCE IN PRECISION OF ORIENTATION

The deviation produced by a prism is necessarily rather insensitive to changes in angle of incidence, i, under the conditions which obtain when the prism is at or near the position of minimum deviation. This fact is quantitatively shown [24] by the equations

$$\frac{dD}{di}=0$$

and

$$\frac{d^2D}{di^2}=2\tan i\left(1-\frac{\tan^2 A/2}{\tan^2 i}\right) \tag{10}$$

from which, using Taylor's theorem, it is possible to express [25] the relationship

$$\Delta D=\tan i\left(1-\frac{\tan^2 A/2}{\tan^2 i}\right)\Delta i^2 \tag{11}$$

which exists between small departures from minimum deviation and errors in orientation. Upon substituting for ΔD of equation (11) the appropriate elemental tolerance (in radians), namely, one-half of that expressed (in seconds) by equation (3), there results

$$\Delta i^2=\frac{2\times 10^{-6}\tan\left(\frac{A+D}{2}\right)}{n\tan i\left(1-\frac{\tan^2 A/2}{\tan^2 i}\right)}$$

and, since at minimum deviation i is identical with $(A+D)/2$ and $\sin A/2=n^{-1}\sin i$, one readily finds a particular value of Δi which may be expressed as the tolerance

$$T'_{\Delta i}=\pm 4.86\cos A/2\left(\frac{n}{n^2-1}\right)^{1/2}\text{ minutes} \tag{12}$$

which applies to each of the two prism orientations involved in a single observation of 2 D.

It is seldom possible, however, to obtain desirably precise results from a single observation of minimum deviation, and the errors which

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[22] For both exhibits of Figure 4 the median and the mode are slightly negative with respect to the mean but the quantitative measures of the asymmetry which were calculated from the third moments, although positive in both cases, scarcely exceed their standard errors. For curves E and F, respectively, the values are $+0.10\pm0.09$ S. D. and $+0.12\pm0.13$ S. D.

[23] The quantitative measures of the symmetrical departure from the normal form, as calculated from the fourth moments, are negative in each case, but for curves E and F, respectively, the values are only -0.31 ± 0.18 S. D. and -0.09 ± 0.25 S. D. Moreover, the use of Elderton's Table of Goodness of Fit gives probabilities of 0.23 and 0.73, respectively, for these curves and thus indicates that the data conform to a normal distribution about as well as could be expected if the samples were taken from a perfectly normal universe.

[24] See, for example, J. P. C. Southall, Geometrical Optics, p. 82; 1910 (New York). There, however, in the last equation on that page, 2 tan $\beta/2$ should appear instead of sin β.

[25] Assuming sufficiently small departures from the minimum-deviation prism position, equation (11) agrees with Cornu's expression for excess deviation (Annales de l'Ecole Normale Superieure (2), **9**, p. 100; 1880).

are decreased directly as the square root of the number of observations are not the errors in deviation, but are those errors which are made in average azimuth of the prism. This average azimuth rapidly approaches the correct azimuth but it does not, however, have any comparable corresponding value of the deviation. Consequently the useful tolerance to establish, when investigating this error in minimum-deviation refractometry, is not one for a single error in prism orientation or for an average orientation but a tolerance which relates properly to one-half of the average departure from double minimum deviation,[26] namely, to $\Sigma\Delta D/N$. Since the values of Δi correspond to a normal distribution of residuals, a suitable tolerance is easily found. This becomes apparent when the process of summation is applied to equation (11) in evaluating the average departure

$$\frac{\Sigma\Delta D}{N}=\tan i\left(1-\frac{\tan^2 A/2}{\tan^2 i}\right)\cdot(1.483\ P.\ E.\ i)^2 \qquad (13)$$

in minimum deviation. The quantity $\Sigma\Delta i^2/N$ is, for a normal distribution, the second power[27] of the "standard deviation" or "error of mean square" and thus is expressed as $(1.483\ P.\ E.\ i)^2$, where $P.\ E.\ i$ is the probable error of a single orientation of the prism. Then from equations (3) and (13) one finds the tolerance

$$T_{P.\ E.\ i}=\pm 3.28\cos A/2\left(\frac{n}{n^2-1}\right)^{1/2}\text{ minutes} \qquad (14)$$

which is required in the precision of a series of $2N$ prism orientations, namely, a tolerance which corresponds to an absolute error of $+1\times10^{-6}$ in the index resulting from one-half the average of all of the N measured values of double minimum deviation. From equation (14) there have been computed the values which are plotted in Figure 5 to show, for a wide range of refractive angle, the variation in this tolerance for work on media of various indices.

3. CORRECTION FOR PRISM-ORIENTATION ERROR

Because the investigations of prism-orientation error which are reported in this paper were made by a single observer; and, because of the variety of possible instrumental and observational conditions under which minimum-deviation measurements may be undertaken, the results are not sufficiently extensive to permit of conclusive, wide generalization. As has been mentioned, however, these orientation errors are simply related to pointing errors and certain unpublished data show that a second observer's pointing errors are at least as small as those on which this paper is based. Therefore, it appears that one may easily so arrange the working conditions that special orientation procedures are unnecessary in sixth decimal place refractometry.

Consequently, before adopting a special program for increased accuracy in orientation under any given set of experimental conditions, it is advisable to determine by N observations the probable error of a

[26] The deviation observed is $2D$, but the systematic departure therefrom, due to the two prism orientations, is $2\Delta D$ and not $\sqrt{2}\Delta D$ (where ΔD is the departure from minimum deviation for a single prismorientation), because, as previously mentioned, every ΔD has a positive sign. Hence, one-half of the average departure from double minimum deviation is simply $\Sigma\Delta D/N$.

[27] See a text on error theory; for example, E. T. Whittaker and G. Robinson, The Calculus of Observations, p. 182; 1924 (London).

single prism orientation by ordinary hand adjustment and then to use Figure 5 for determining the sufficiency of the precision which is thus attainable. In fact, an observer who has initially determined, with a given spectrometer, his probable error in prism orientation for various spectral lines and prism sizes may thereafter consult the curves of Figure 5 and apply the proper index corrections. For the orientation precision shown by the curves, the correction is -1×10^{-6} in index and for other values of the precision the correction varies directly as $(P.\ E.\ i)^2$.

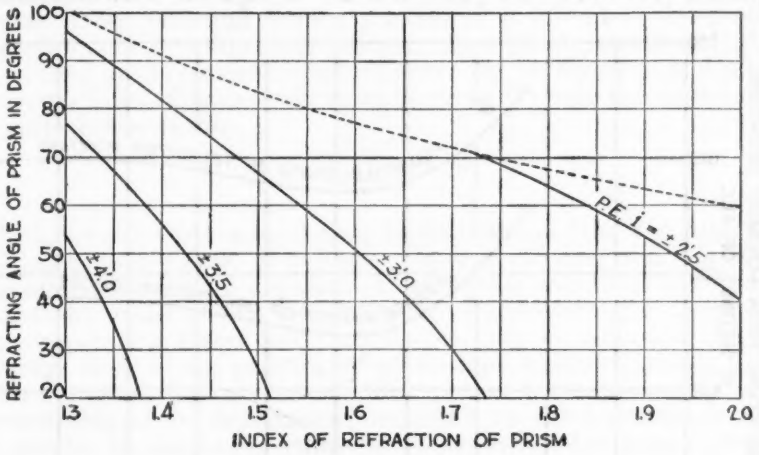

FIGURE 5.—*Iso-tolerance curves, in minutes of arc, for precision in orientation of prism*

In order that the systematic prism orientation error in the index of refraction, as computed from one-half the average of N observed double minimum deviations, shall not exceed $+1\times10^{-6}$, it is necessary that at least one-half of all individual errors in orientation, Δi, shall not exceed the tolerance which may be read from this figure. The contours for these probable errors of single orientations were computed from equation (14). The dotted line is that of the limiting condition, $A=2$ arcs in n^{-1}, at which both incident and emergent light grazes the prism surfaces. When seeking a certain degree of accuracy in index measurement under any given experimental conditions the probable error in orientation by simple hand adjustment should be determined and the curves of this figure may then be used either for determining the absolute value of the negative correction which should be applied to the index or for reaching a decision concerning the necessity of using more precise methods for orientation adjustment.

Although the repetition of observations has no systematic effect on the error in index which results from incorrect orientations, it does permit increased reliance on the computation of the absolute value of such errors; that is, the accuracy of index corrections, made in the manner suggested, is a function of the number of independent observations.

V. PRISM SIZE AND SIMPLE ORIENTATION PROCEDURE

It is suggested in Section IV, 1, (*a*) that there may be a definite connection between the precision of prism orientation and the precision of telescope pointing. Such a relationship, if known, can be used in determining what size of prism should be adequate for use in sixth decimal place refractometry without resorting to the correction discussed in the preceding section.

1. RELATION OF POINTING ERROR TO SYSTEMATIC DEPARTURES FROM MINIMUM DEVIATION

The quantitative evaluation of this relationship is, however, complicated by the fact that the systematically positive departures from minimum deviation (as caused by errors in orientation) can not[28] follow a normal error distribution curve such as may safely be assumed for the accidental errors of telescope pointing. The departures from minimum deviation which correspond to experienced values of the probable error in orientation might, of course, be computed by equation (11) and a curve, similar to D_1' of Figure 6, be so determined.

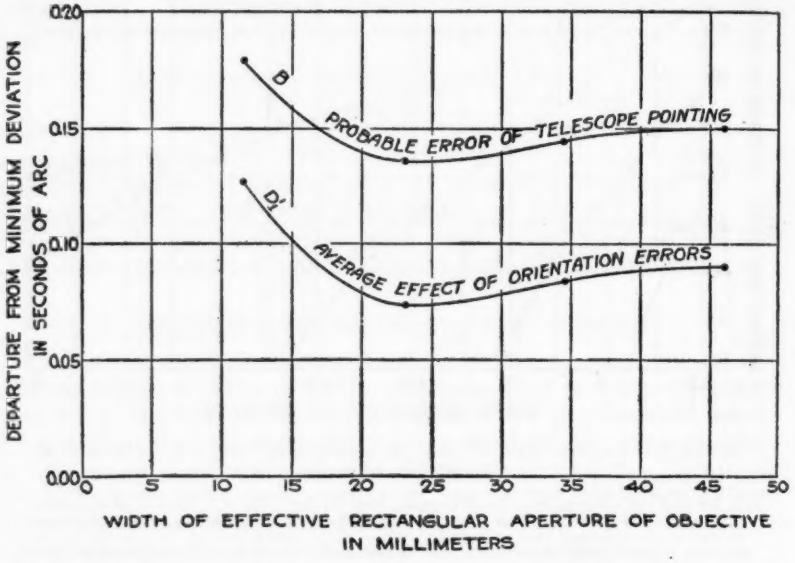

FIGURE 6.—*Comparative effects of pointing and orientation errors on minimum deviation*

Curve B is reproduced from Figure 1, and D_1' is computed from curve D_1 of Figure 2 by means of equation (13). From a comparison of the ordinates of these curves it appears that the average systematic effect of prism orientation error is equal to 0.6 of the absolute value of the probable error of a single telescope pointing.

Its ordinates would average less than one-third of those of curve B, as drawn in Figure 1 and reproduced in Figure 6. This result signifies that 50 per cent of all individual departures from minimum deviation are less than one-third the probable error of a single telescope pointing. If, however, the root mean square error in orientation is taken as the basis of comparison, the relative heights of the resulting curves would be different, the ordinates of the "D" curve being in this case about one-half of those for the comparable "B" curve. It seems, in fact, from further similar analysis of the experimental data that approximately 99 per cent of all errors in simple prism orientation do not cause departures from minimum deviation in excess of a limiting angular value which also includes 99 per cent of the optical errors in telescope pointing.

[28] Equation (11) considered in connection with the equation for normal error distribution shows that ΔD and Δi can not both be normally distributed, and it has been shown in Section IV, 1, (c) that the values of Δi follow a normal curve.

Under these circumstances it appears that no single comparison of the levels of curves, such as B and D_1' is of general utility. Allowing for experimental error, however, the last mentioned or 99 per cent comparison may be considered as definite quantitative evidence of a significant relationship. It shows that the limiting errors in the (optical) pointing of a telescope are also the limiting departures from minimum deviation which are caused by simple orientation procedures. In the present investigation a more directly useful relationship to establish is that between the probable error in telescope pointing and the arithmetical average of the departures from minimum deviation, since the latter is an actual error which affects an index measurement resulting from a number of independent orientations for minimum-deviation observations. Accordingly, equation (13) has been used in the computations for curve D_1' of Figure 6, and a comparison of its ordinates with those of curve B yields the approximate empirical relationship

$$\frac{\Sigma\Delta D}{N}=0.6\ m \tag{15}$$

which, for the various apertures, exists between (the absolute value of) the probable error of a single telescope pointing and one-half of the average (positive) departure from double minimum deviation as caused by errors in prism orientation. Incidentally, the distribution of the pointing errors being normal, it may be remarked that the average error in the pointing of a telescope is approximately 1.2 m. Thus equation (15) gives some idea of that favorable nature of the distribution of the departures from minimum deviation which makes it possible by simple procedures to statistically select prism azimuths that are intermediate between those positive and negative limiting positions which are barely perceivable as erroneous.

2. SUITABLE AND SUFFICIENT PRISM SIZE

For the purpose of determining prism size, the most readily useful measure of the precision of a series of prism orientations is the simple arithmetical average of the resulting departures from minimum deviation and this average value, $\Sigma\Delta D/N$, has been related to pointing error by equation (15).

Consequently, from equations (1), (4), and (15) the average departure from double minimum deviation, arising solely from N prism orientations at each of the two observational positions involved in N determinations of double deviation, is

$$\frac{2\Sigma\Delta D}{N}=\frac{25\times 10^4 K\lambda}{L\cos i}\ \text{seconds.} \tag{16}$$

In obtaining equation (16) the radical sign is removed from the factor $\sqrt{2}$, as used in the numerator of equation (5), because the departures from minimum deviation are of positive sign at the orientations for both right and left observational positions. Moreover, this average departure, unlike the error expressed by equation (5), is independent of the number of observations. This is a strictly fundamental limitation to which reference has already been made in Sections III, 2 and IV, 3. It may be noticed that this empirical result, equation (16),

when compared with equation (5), indicates that, in general, the systematic prism-orientation error in double deviation is not very different in absolute value from the combined probable error of the two (optical) pointings in a single determination of double deviation.

By again imposing suitable tolerance conditions, as was done in treating the special case expressed by equation (8), the right-hand members of equations (3) and (16) may be equated to give

$$L_D = \frac{30 \times 10^4 K\lambda}{\sin A/2} \tag{17}$$

as the general expression for an appropriate and sufficient value for length of prism surface. Incidentally, it may be remarked that equation (17), considered together with Figures 1 and 2 of the paper first above cited,[29] shows a further advantage of using prism angles of more than 60° when working on media of low refractive index.

If, as in Section III, it be again assumed that the magnification, the contrast conditions in the image, and the aberration of the prism, are consistent with a normal value of K, then the proper value of L for use in sixth decimal place index measurements by the usual practices of the minimum-deviation method is determinable. Using for K the value of 1/25 and again considering the longer wave lengths of the visible spectrum, it is evident that an approximate value is

$$L_D = \text{cosec } A/2 \text{ centimeters.} \tag{18}$$

For 60° prisms of any refracting medium it is thus unnecessary, when making deviation measurements, to use prisms with a length of surface exceeding 2 cm unless it is desired to limit all of the various individual [30] errors to something less than approximately $\pm 1 \times 10^{-6}$ in their effect on the computed index of refraction.

WASHINGTON, October, 1930.

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[29] See footnote 1, p. 60.

[30] In this investigation the various limits and tolerances are not considered collectively but are established individually at values consistent with errors of $\pm 1 \times 10^{-6}$ in index of refraction. It is, of course, recognized that this procedure is not adequate for accurate sixth decimal place refractometry; but, with a few repetitions in the observations, the approximation is very good.

RP263

OPTIMUM USE OF MATERIAL IN BIOLOGICAL ASSAYS

By Warren W. Nicholas

ABSTRACT

It is shown that the procedure often adopted in biological assay to determine the mortality-dosage curve is very wasteful of animals and of time. The available animals are usually divided into equal groups to which are administered various doses which differ in strength by equal steps; the inefficiency is due to the fact that various points on the curve are determined with different degrees of accuracy. A method is described which will determine the curve with uniform accuracy throughout its extent—here the animals are divided into unequal groups, in which the relative numbers are described by a simple mathematical expression.

The case usually encountered in routine biological assay where a single point on the curve is to be determined (that is, corresponding to a biological test for strength of a preparation) is also treated. A method is described which makes the best use of a given number of animals, and permits the results to be expressed quantitatively.

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I. INTRODUCTION

In biological assay, in order to specify the amount of drug (or other effective agent) required to produce a certain effect (say mortality) in a given organism, it is customary to specify a dosage (D_o) of the agent which produces the "end-point" effect in a certain specified percentage of the organisms in a group sufficiently large in number to reduce the probable errors to a small quantity. The necessity for such a way of specifying dosage is apparent from a consideration of what will here be called after Trevan [1] the "characteristic curve," which describes the effect of various doses of the effective agent on the organisms. A characteristic curve which is approximated in a great majority of such reactions is shown in Figure 1; here "survival" (that is, fraction of organisms in which the agent did not produce the end-point effect) is plotted as ordinates, and dosage (D) as abscissæ.[2] It is seen that even doses which are a small fraction of D_o can produce

[1] J. W. Trevan, Proc. Roy. Soc., B. 101, p. 483; 1927. Trevan's treatment of the errors associated with the determination of toxicity closely parallels that in the present paper at many points, but Trevan did not discuss the present applications explicitly.

[2] It may be pointed out that, if desired, D may represent throughout the present paper the dose per unit susceptibility of an animal instead of the actual dose per animal; that is, corrections for weight, sex, etc., may be made without affecting the results of the paper so long as the meaning of D is consistent throughout the calculations of any one experiment. (For example, if the Dreyer-Walker correction for weight held, the dose administered to an animal might be taken to be $DW^{.66}$ where W is the weight of the animal, and D is the quantity appearing in the equations of the paper.) It is obvious, however, that any statistical analysis such as is given here will be valid whether such corrections are made or not, since the neglect of the corrections will simply superpose another random variation upon the variations already existing; the characteristic curve will, of course, be broadened by the neglect of such corrections.

the effect in a fraction of the organisms, and that even for doses considerably in excess of D_o, the effect is not produced in all the organisms. The cause for this large degree of variability in the reactions of the different individuals is not yet ascertained, but in any event, this uncertainty as to the underlying cause is no factor in the present discussion.

A great number of organisms is required to determine D_o with any considerable degree of certainty, and there has been considerable criticism of the paucity of material used in many assay experiments. But even when a large amount of biological material (as for example, a large number of animals and correspondingly large amount of drug) has been used, it is often questionable whether the best use has been made of the material. For example, suppose the characteristic curve has been ascertained using, say, eight different values for the dose of poison

$$\frac{1}{4} D_o, \frac{1}{2} D_o, \frac{3}{4} D_o \quad . \quad . \quad . \quad . \quad . \quad . \quad 2 D_o$$

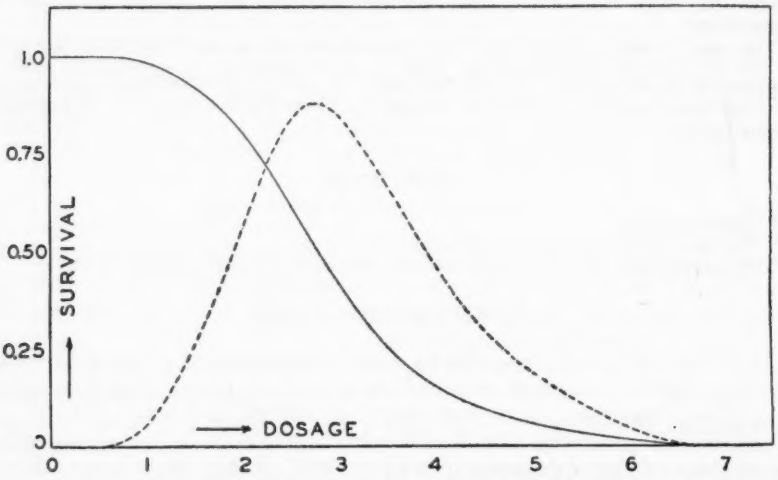

FIGURE 1.—*Typical characteristic curve, with best distribution of counts*

Continuous line, "characteristic curve" (see text) which is approximated in a majority of biological reactions dealing with mortality due to X rays, ultra-violet light, and various toxic agents, physiological effects of hormones and vitamins, and hemolysis due to specific sera. Broken line, best distribution of individual organisms or counts for determining the characteristic curve with uniform accuracy along its length.

where D_o is in this example the dose required to kill half the animals, and giving to one-eighth of the total number of animals each respective value of the dose. Then for the characteristic curve ordinarily obtained it can be shown that with the ordinary use of the data found (that is, without special weighting), more than half ot the animals and poison have been wasted so far as an exact determination of the characteristic curve is concerned, and the experiment could have been done just as accurately with less than half of the animals and poison, or could have been done 1.4 times as accurately using all the material.[3]

[3] The above point is entirely apart from the consideration that, for a given experimental uncertainty in the dose administered to an animal, the uncertainty thereby caused in the mortality is greatest at the steepest point on the characteristic curve. This latter effect is not discussed in the present paper; but a correction for the effect is readily made once the uncertainty in the administered dose is known.

It will be shown below that, where the dosages are uniformly distributed along the axis of abscissæ, as in the above example, the best use of material is made by dividing the animals into unequal groups (instead of equal, as in the example above), the group containing the largest number being given the dose which will kill half of them and the groups becoming continually smaller for both increasing and decreasing doses. The quantitative relation which will be found for the optimum use of material (assuming it is desired to obtain all points on the characteristic curve with equal accuracy) is

$$\frac{n}{n_o}=\frac{s(1-s)}{0.25} \tag{1}$$

where n is the number of individuals in the group given a dosage for which the fractional (not percentage) survival is s, and n_o is the number in the group given a dose for which s is 0.50. It is apparent, from the fact that survival is equal to 1 minus the mortality (m), that the numerator of the fraction on the right-hand side can be written in two other ways, namely, sm and $m(1-m)$. The curve corresponding to this formula, as applied to the characteristic curve shown in Figure 1, is given in the broken curve of Figure 1.[4]

In cases where any number of organisms and any amount of the effective agent are available, it is not necessary to have regard to the optimum use of material. However, even in these cases, it often happens that the administration of the agent or the counting of the affected and surviving organisms is tedious or difficult; in this event, the analysis given below is of as much value as in the experiments in which a saving of material was important, the difference being that here a saving of time and trouble is effected. An example of experiments tending toward the latter type are those of Packard on the effects of X rays on Drosophila eggs. Here a great number of eggs were used in order to obtain high precision in a test of certain quantitative theories for the nature of the biological action of the rays. In fact, the present investigation was suggested by an observation of Packard's that certain points on the characteristic curve seemed to have associated with them a greater uncertainty of determination than others.[5]

The analysis contained in the present paper applies to a great many biological reactions—in fact to every kind in which the independent variable is the quantity or concentration of some effective agent, such as X rays, ultra-violet light, many toxins and inorganic drugs, hormones, vitamins, specific sera, etc., and the dependent variable is the percentage of cases in which a given end-point effect is produced in a group of individuals, this effect being of the nature of something (such as mortality, hemolysis, production of oestrus, etc.), which can either happen or fail to happen to an individual. The first part of the paper deals with the best distribution of animals

[4] In the past it has sometimes been the practice to mark on the graph the number of animals used for the determination of each point. In the future it will be sufficient to specify the total number of animals used for the entire graph, and to say that they were distributed according to the relation $m(1-m)$. The dosages used will be evident from the points plotted on the graph.

[5] Charles Packard, J. Cancer Res., **11**, p. 1; 1927. Packard interpreted his observation that the greatest uncertainties were associated with mortalities in the region of 50 per cent as signifying that a greater degree of biological variation was associated with organisms which were susceptible to the range of doses in the vicinity of that which produced a 50 per cent mortality. As will appear below, however, this interpretation can not be accepted without further analysis of the experimental data in terms of the present results.

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to use in case the characteristic curve is known approximately, and it is desired to ascertain it more accurately, as has been the case, for example, in Packard's experiments cited above. The second part of the paper deals with the more usual case in biological assay where it is not so important to determine the whole curve, but only one point on it, for example the dose required to produce 50 per cent mortality. The reason for discussing the two parts of the paper in this apparently inverse order is because some of the formulas to be developed in the first part of the paper will be needed in the second part.

II. TO DETERMINE THE ENTIRE CHARACTERISTIC CURVE

Any determination of an "optimum use of material" in the present sense implies such a use of material as involves the least error in the final result, as indicated by statistical analysis. In order to make familiar the application of statistics to the present problem, let us first consider a special numerical case. Suppose an individual organism be given a dose D_o of some effective agent, say a poison. If, for example, this dose is that which will kill half of any very large group of similar organisms, we may conclude that the individual which we have selected at random will have an equal chance of dying (+) (that is, that we will obtain a positive effect) and surviving (−). We may represent this state of affairs by the symbolization.

\+
−

giving, in our minds, equal "weights" to both. Suppose next that two individuals, A and B, are each administered D_o; A has as before equal chances of + and − . Whether A dies or not does not affect the reaction of B, so that there are equal chances, when A dies, of B's dying and surviving; this may be represented by + + and + −. By similar reasoning we can show that the other two possibilities, − + and − −, are equal, and also that + − is equal to − −. Thus we have finally four equally probable possibilities for the effect of D_o on two individuals

\+ +
\+ −
− +
− −

The above reasoning may be nicely symbolized and the results extended to any number of individuals as follows:

One individual	Two individuals	Three individuals	Four individuals
+	+ + + −	+ + + + + −	+ + + + + + + −
−	− + − −	+ − + + − −	+ + − + + + − −
		− + + + − −	+ − + + + − − −
		− + − −	− + + + − − −
			− + + − − − −
			− − + + − − − −
			− − − −

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It follows immediately, from an enumeration of the various possibilities in the above representation, that with two animals the chance of zero mortality is 0.25, the chance of 50 per cent mortality is 0.50, and the chance of 100 per cent mortality is 0.25; with three animals, mortalities of 0, 33⅓, 66⅔, and 100 per cent correspond, respectively, to probabilities 0.125, 0.375, 0.375, and 0.125. A graphical representation of these probabilities, among others, is given in Figure 2.

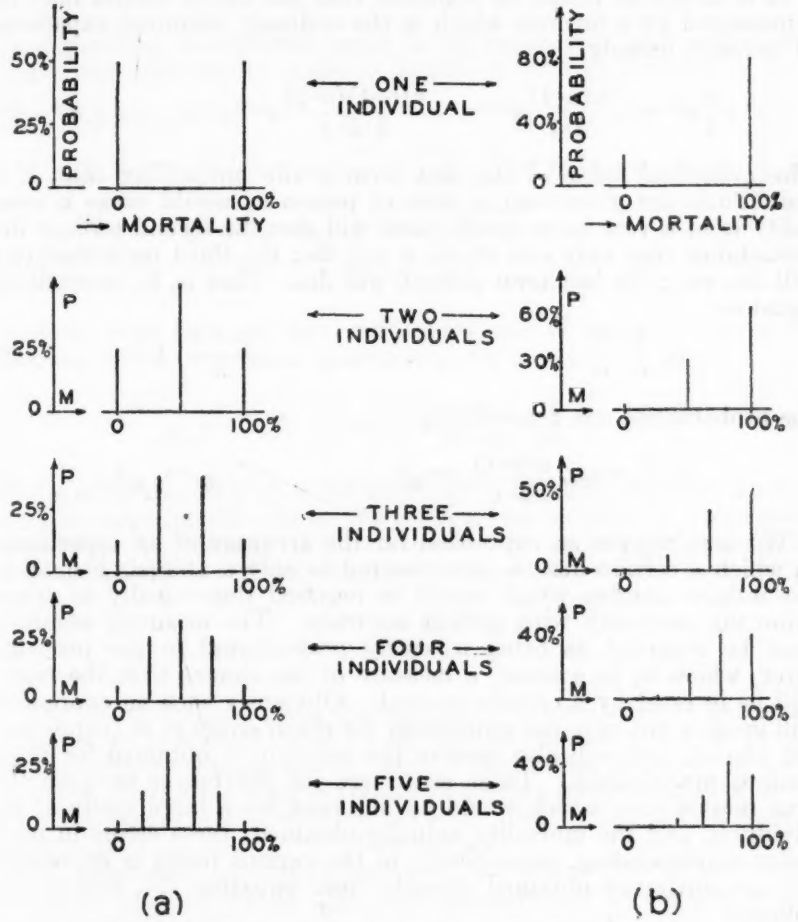

FIGURE 2.—*Some probabilities for mortality in small groups*

Probabilities of obtaining various values for mortality in experiments on small numbers of individuals (*a*) for doses of poison which would kill 50 per cent of a very large group of individuals, and (*b*) for doses which would produce 80 per cent mortality in a large group.

Figure 2 (*a*) represents the case for a dose D_o, as was illustrated above, and Figure 2 (*b*) gives the result for a larger dose of poison, one which would kill 80 per cent of the individuals in a large group. The method of getting results for dosages other than D_o will be outlined below. It must be clearly understood that, although the above analysis signifies, for example, that if eight groups, with three individuals in a group, were given a dose of poison D_o, the most probable

result would be that one group would entirely survive, one would entirely die, three groups would have only one death each, and three other groups would have only two deaths each, it does not signify that this result will always be obtained in practice; in fact it is one purpose of the present paper to find how in practice the chance of obtaining the most probable result varies with the number of individuals treated.

It is shown in books on statistics that the above results may be represented by a formula which is the ordinary binomial expansion of $(s+m)^n$, namely

$$s^n+\frac{n}{1}s^{n-1}m+\frac{n(n-1)}{2\cdot 1}s^{n-2}m^2+\frac{n(n-1)(n-2)}{3\cdot 2\cdot 1}s^{n-3}m^3+\ldots+m^n \quad (2)$$

The numerical value of the first term is the probability that, if n individuals are given such a dose of poison as would cause a mortality m in a very large group, none will die; the second term is the probability that only one of the n will die; the third term that two will die, etc.; the last term that all will die. That is, for mortalities equal to

$$0, \frac{1}{n}, \frac{2}{n} \ldots\ldots\ldots\ldots \frac{n-1}{n}, 1 \quad (3)$$

the probabilities are, respectively

$$s^n, \frac{n}{1}s^{n-1}m, \frac{n(n-1)}{2\cdot 1}s^{n-2}m^2 \ldots\ldots \frac{n}{1}sm^{n-1}, m^n \quad (4)$$

We next require an expression for the accuracy of an experiment in which a certain dose is administered to only n animals instead of the infinite number which would be required theoretically to determine the mortality with perfect accuracy. The accuracy obtained may be regarded as being inversely proportional to the probable error, which is, in a sense, a measure of the chance that the result will be in error by a certain amount. Obviously such an expression will involve not only the probability for given errors in m (expression (4) above), but will also involve the errors in m obtained for these various probabilities. These errors are the differences between the true mortality m which would be observed for a large group of individuals, and the mortality actually obtained; these errors in mortality corresponding, respectively, to the various terms in expression (4) are obviously obtained directly from equation (3), and are as follows:

$$m, m-\frac{1}{n}, m-\frac{2}{n} \ldots\ldots\ldots\ldots m-\frac{n-1}{n}, m-1 \quad (5)$$

An expression for σ, the mean error in the mortality (or the "standard deviation" of statistics), in conformity with customary usage is the following:

$$\sigma=\sqrt{\frac{\Sigma P(\Delta m)^2}{\Sigma P}} \quad (6)$$

where P represents a term of formula (4) and Δm represents the corresponding term of formula (5) and Σ signifies that a summation is to

be made over all terms of the formulas. Substituting from the formulas, we have

$$\sigma^2 = \frac{s^n m^2 + \frac{n}{1} s^{n-1} m\left(m - \frac{1}{n}\right)^2 + \frac{n(n-1)}{2 \cdot 1} s^{n-2} m^2 \left(m - \frac{2}{n}\right)^2 + \cdots + m^n (m - 1^2)}{s^n + \frac{n}{1} s^{n-1} m + \frac{n(n-1)}{2 \cdot 1} s^{n-2} m^2 + \frac{n(n-1)(n-2)}{3 \cdot 2 \cdot 1} s^{n-3} m^3 + \cdots + m^n}$$

or, expanding the squared terms in the numerator, and noting condensations that can be made by means of formula 2 above

$$\sigma^2 = \frac{\begin{array}{l} m^2 (s+m)^n \\ -2m^2 \left[s^{n-1} + \frac{n-1}{1} s^{n-2} m + \frac{(n-1)(n-2)}{2 \cdot 1} s^{n-3} m^2 + \cdots + m^{n-1} \right] \\ + \frac{m}{n} \left[s^{n-1} + 2 \frac{n-1}{1} s^{n-2} m + 3 \frac{(n-1)(n-2)}{2 \cdot 1} s^{n-3} m^2 + \cdots + n m^{n-1} \right] \end{array}}{(s+m)^n} \quad (7)$$

Now we note that the first and second sets of terms in the square brackets above are equal, respectively, to

$$\frac{1}{n} \frac{\partial}{\partial s} (s+m)^n \qquad \text{and} \qquad \frac{1}{n} \frac{\partial}{\partial m} \left[m \frac{\partial}{\partial s} (s+m)^n \right] \quad (8)$$

this is easiest verified by differentiating the expanded form of $(s+m)^n$. Finally operating directly on the unexpanded binomial in the manner prescribed by formula (8), substituting in equation (7), reducing algebraically, and remembering that $s+m=1$, we readily find

$$\sigma = \sqrt{\frac{sm}{n}}$$

The above formula gives the mean error associated with the determination of any single point on the characteristic curve (that is, corresponding to some particular value of the dosage or poison or other effective agent, or to some particular concentration in which the organisms are placed, etc.), where n is the number of individuals used in determining the point. The formula shows, for example, that if an equal number of individuals were used for each point, the mean error would be proportional to $\sqrt{sm}$; this quantity will be a maximum for $m=s=0.5$; that is

$$\frac{d}{dm}\sqrt{sm} = \frac{d}{dm}\sqrt{m(1-m)} = 1/2(m-m^2)^{-\frac{1}{2}}(1-2m) = 0, \text{ or } m = 0.5$$

and will approach zero as either m or s approaches zero. This means that with equal numbers of individuals for all points, the points on the curve corresponding to values of m close to 0 and to 1, will have been obtained much more accurately than points for which m is in the neighborhood of 0.5. But for purposes of constructing a graph, there is usually no purpose in determining one point more accurately than any other; the accuracy of a graph may be ordinarily considered to

be no greater than that of its least accurately determined region. Therefore, more individuals than necessary have been used to determine all the points except that for which $m=0.5$.

For a more efficient use of material, we may assume that, unless there happens to be some reason to the contrary, in a particular experiment, it is desired to obtain all parts of the characteristic curve with equal accuracy. Suppose the usual procedure has been adopted, wherein doses are given which are equally spaced on the axis of abscissæ,[6] then the above condition of equal accuracy can be met by distributing the individuals among the various points in such a fashion as to make the mean error associated with any point equal to that associated with any other point. That is, we wish to make σ in equation (9) above equal to some constant, say $(4n_o)^{-1}$.[7]

$$\sigma=\sqrt{\frac{sm}{n}}=\sqrt{\frac{1}{4n_o}}$$

whence

$$\frac{n}{n_o}=4sm=4m(1-m)=4s(1-s) \tag{10}$$

which appeared as equation (1) in the introduction.[7]

III. TO DETERMINE THE DOSE REQUIRED TO PRODUCE A GIVEN MORTALITY

If, as in many practical problems of biological assay, it is not required to determine the entire characteristic curve, but only the dose D_o which will produce the end-point effect in a certain previously specified fraction $m_o(=1-s_o)$ of a group of individuals, a still more efficient use can be made of the available material. The method is dependent on the fact that, even if only a very small group of individuals is administered a dose of the effective agent, and the survival found, a most probable value for D_o can be calculated at once from the characteristic curve,[8] and also the probable error associated with this result. If this probable error is too large, a different dose (and the method specifies what will be best to use next) may be administered to another small group, and again the most probable value for D_o (with associated probable error) calculated making best use of the results from both sets of animals used so far. If this second probable error is still too large, the process may be repeated as often as necessary, the progress of the experiment always being guided in the best manner by all data secured up to that stage, and the final result always making best use of all data and specifying the accuracy quantitatively.

[6] The proper construction of a segment of a curve from a set of observed points is in reality influenced by all the points in the immediate vicinity of the segment. Therefore, if the values for the dosage were grouped closer together in one region than in another, the curve would ordinarily have been determined with greater accuracy in the former region. A uniform distribution is chosen above for simplicity.

[7] It might appear to have been better to replace n by $n-1$ in these formulas, as is shown in the theory of errors to be necessary in a calculation of mean error involving the arithmetic mean of the observations instead of the true value of the quantity to be determined (that is, corresponding to *à posteriori* probabilities). However, it is here supposed that the mean errors for the various observed points (and thus the optimum distribution of material) are calculated from the smoothed characteristic curve (or its preliminary determination). Here the ordinates for any region of the curve are really influenced by all determined points in the vicinity, and thus the value for n which is effective in this regard is much greater than the value of n used for any one point on the curve, and the fractional difference between n and $n-1$ becomes negligible.

[8] In ordinary routine assay work, the shape of the curve is known accurately, and it is merely desired to find the potency of a given preparation; this corresponds to determining the scale of abscissae for that preparation. When the curve is not known, the above method may still be of considerable value if a reasonable shape for the curve be assumed.

In order to describe the calculations required above, let us consider any one, say n_k, of the small groups of individuals, n_a, n_b, n_c . . . . which may be used in the experiment: Suppose a survival s_k is found for this group when a dosage D_K is administered to each individual. So far as can be determined from only this single isolated part of the experiment, s_k is the most probable value of the ordinate on the characteristic curve corresponding to abscissa D_K, and the most probable value of D_o, say D_k, is found by simply noting the position of s_k on the characteristic curve and multiplying D_K by such a ratio as will appear to have produced a survival of s_o instead of s_k ($s_o=1-m_o$; see above). If the characteristic curve be represented by the relation $D=f(s)$, this calculation of D_k may be described symbolically as follows:

$$D_k=D_K\frac{f(s_o)}{f(s_k)} \tag{11}$$

To find the probable error associated with D_k, we note first that the probable error associated with s_k is

$$\Delta s_k=0.6745\sqrt{\frac{s_k(1-s_k)}{n_k-1}} \tag{12}$$

this is the same as formula (10) except for a change in the denominator of the fraction as discussed in footnote 7 and the necessary change from mean to probable error. When s varies along the characteristic curve from $s_k-\Delta s_k$ to $s_k+\Delta s_k$, D obviously varies from $f(s_k-\Delta s_k)$ to $f(s_k+\Delta s_k)$; for the purposes of the present paper,[9] the probable error ΔD_k to be associated with D_k may be taken to be

$$\frac{f(s_o)}{f(s_k)}\cdot\frac{f(s_k-\Delta s_k)-f(s_k+\Delta s_k)}{2} \tag{13}$$

The fraction on the right above is the error associated with D_K, and the purpose of the fraction on the left is simply to cause D_k to have the same percentage error as D_K.

Now, to begin the experiment, an arbitrary dose D_A is given each individual in a small group, n_a, the survival, s_a, is noted, and the probable value, D_a, of D_o with its associated error, ΔD_a, is calculated as above.[10] (For additional clarity, an example of these calculations is given in fig. 3.) If ΔD_a is too large, we give each individual of a

[9] It may be pointed out that the method described by equation (13) for the calculation of ΔD_k from Δs_k is only a special case of a more general method. For example, instead of finding ΔD_k from $f(s_k-\Delta s_k)$ and $f(s_k+\Delta s_k)$ we might have found $R\,\Delta D_k$ from $f(s_k-R\Delta s_k)$ and $f(s_k+R\Delta s_k)$, where R is a constant the value of which is a matter of choice. When R is relatively small, when s_k lies on a relatively straight portion of the graph, and when the determination of s_k is relatively accurate (that is, when Δs_k is small), the value found for ΔD_k will not depend appreciably on R; on the other hand, when the graph is strongly curved, etc., ΔD_k depends on R. It may be pointed out further that when $s_k-R\Delta s_k$ is equal to or less than zero, or when $s_k+R\Delta s_k$ is equal to or greater than 1.0, ΔD_k becomes infinite, and consequently the result with the group of animals n_k is discarded so far as its effect on the probable error of the final result is concerned. (See Equation (14).) Both of these features are believed to be desirable, and the choice $R=1$ seems a reasonable value to select, although for some purposes other values of R may be found to be preferable.

[10] The degree of success attained with the above method depends to some extent on the determination of the first dose to be given, D_A. For the closer D_A happens to approximate D_o, the fewer individuals will be required to attain a certain accuracy of determination of D_o. For example, until a value for D_A is found which gives s_a a value different from either zero or 100 per cent (that is 1.0), no definite statement can be made about the most probable value of D_o; that is, mathematically, the value D_o is indeterminate. However, the special case in which nothing whatever is known about the approximate magnitude of the dose required to produce a known end-point effect is seldom encountered in practice. When it is encountered, the method usually followed when animals are valuable is to administer gradually increasing doses to a single animal, making some kind of allowance for a possible adaptation.

second group, n_b, a dose $D_B = D_a$, and as before find D_b and ΔD_b. As is shown in the theory of errors, we may combine the results of the two experiments, and find that the most probable value for D_o is now

$$D_C = \frac{D_a/(\Delta D_a)^2 + D_b/(\Delta D_b)^2}{1/(\Delta D_a)^2 + 1/(\Delta D_b)^2}$$

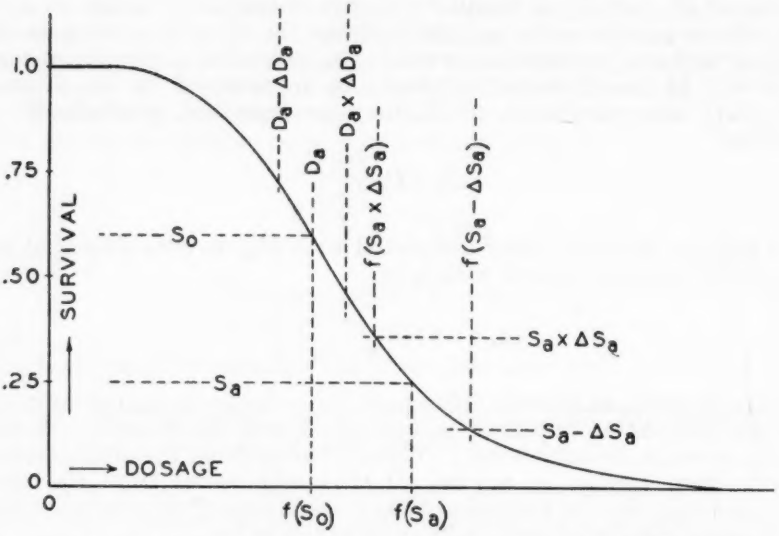

FIGURE 3.—*An example of the assay of a preparation of unknown strength, but for which the shape of the characteristic curve is known*

The strength of a preparation can be described by specifying the dose D_o which would be required to produce its characteristic effect in a fraction s_o (say for example $s_o = 0.60$) of a large number of animals. Suppose a dose D_A is administered to $n_a = 8$ individuals and it is found that 2 do not register the characteristic effect (that is, a survival $s_a = 0.25$ is observed). Then the most probable value D_a for D_o is D_A times the ratio of the abcissae which correspond to s_o and s_a (equation (11)); for example, in the present case $D_a = 0.72\ D_A$.

The probable error (equation 12) in s_a is

$$\Delta s_a = 0.6745\sqrt{\frac{0.25 \times 0.75}{8-1}} = 0.110$$

The values of dosage corresponding to the limits $s_a + \Delta s_a$ (=0.36) and $s_a - \Delta s_a$ (=0.14) are $f(s_a - \Delta s_a) = 1.16\ D_A$ and $f(s_a + \Delta s_a) = 0.90\ D_A$, and the probable error associated with D_A may be approximated with

$$\frac{f(s_a - \Delta s_a) - f(s_a + \Delta s_a)}{2}\ (= 0.13\ D_A \text{ in the present case})$$

Likewise, the probable error in D_a must be $0.13\ D_a$, which is equal to $\frac{f(s_o)}{f(s_a)} \times 0.13\ D_A = 0.09\ D_A$ (compare equation (13)). Thus, finally, $D_o = (0.72 \pm 0.09)\ D_A$ for the case taken here. If this happens to be an undesirably large error, a second group of animals, n_b, may be administered dosages $D_B = 0.72\ D_A$, and so on, as described in the text. In ordinary assay work, where standard numbers of animals are used for n_a, n_b, etc., the above calculations will reduce to a very simple routine.

and that the probable error associated with this value is

$$\frac{1}{\sqrt{1/(\Delta D_a)^2 + 1/\Delta D_b)^2}}$$

We can now give to a third group, n_c, dose D_C, and find D_c, etc., in a similar fashion. In general, after the kth group, n_k, has been given

dose D_K, and D_k and ΔD_k have been found, the most probable value for D_o will be

$$\frac{D_a/(\Delta D_a)^2 + D_b/(\Delta D_b)^2 + D_c/(\Delta D_c)^2 + \ldots\ldots + D_k/(\Delta D_k)^2}{1/(\Delta D_a)^2 + 1/(\Delta D_b)^2 + 1/(\Delta D_c)^2 + \ldots\ldots + 1/(\Delta D_k)^2} \qquad (14)$$

and the probable error associated with this value will be the reciprocal of the square root of the denominator of this expression (14).

I am very much indebted to Dr. Raymond Pearl for consultation and suggestions regarding the above analysis. Also I wish to acknowledge courtesies extended me by the Marine Biological Laboratory at Woods Hole during the preparation of the paper.

Washington, August 30, 1930.

VISCOUS FLOW AND SURFACE FILMS[1]

By Ronald Bulkley

ABSTRACT

This paper describes experiments which have been made on the flow of various liquids through fine glass and platinum capillaries in an attempt to detect any departure from the laws of simple viscous flow. Such a departure could conceivably be brought about by an adsorbed layer on the walls of the capillary or by the attraction of the surface molecules of the walls upon the inclosed liquids. Flow-pressure graphs for various liquids in platinum and in glass capillaries have been obtained. The finest of these capillaries were, respectively, 9.35 and 5.59μ inside radius. The results are in agreement with the laws of simple viscous flow for all of the liquids investigated. Calculations of the radii of the tubes show that the thickness of any immobile adsorbed layer on the walls was not in excess of two to three hundredths of a micron. The diameters of the smallest glass capillaries were measured microscopically and were found to agree satisfactorily with the calculated values.

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I. INTRODUCTION

The distance to which a solid surface is capable of altering appreciably the viscosity of a contiguous liquid is not well known. The practical importance of the problem arises largely from the desire of lubrication engineers to possess more knowledge as to the mechanism of lubrication by very thin films. It is generally accepted that the molecules in the first molecular layer of liquid in contact with the solid are fixed upon the surface molecules of the latter. The feeling of many investigators is that the influence of the solid extends very little further, if any further, than through this first layer of liquid molecules. Other experimenters have observed, however, that liquids have sometimes appeared to possess an abnormally high viscosity when in close proximity to a solid surface. This has led them to the

[1] The substance of this paper was presented as a dissertation to the Johns Hopkins University in partial fulfillment of the requirements for the degree of doctor of philosophy, June, 1930.

belief that orientation and adsorption of liquid molecules may take place in successive layers, and that this effect may continue until a film of relatively great thickness has been built up.

The rate of flow of a liquid through a capillary tube under constant pressure difference is known to vary directly as the fourth power of the diameter of the tube. It should, therefore, not be an insuperable task to detect any considerable effect of the walls upon the viscosity of the contained liquid. If, for example, the effect were sufficient to prevent flow in a layer only a single micron thick adjacent to the walls, then in a tube 0.2 mm inside diameter the observed rate of flow would be 4 per cent lower than the theoretical value. The experiments to be described in the following paper were made in an attempt to detect the influence of the walls of fine glass and platinum capillaries upon the measured viscosity of various liquids which were passed through them.

II. DISCUSSION OF PREVIOUS WORK

Sir William B. Hardy is probably foremost among investigators who favor the view that a solid surface is capable of increasing the viscosity of a contiguous liquid to a relatively great distance. Hardy has done valuable pioneer work in helping to elucidate the perplexing phenomena of boundary lubrication. His conclusions as to the effect of a solid surface upon the viscosity of a neighboring liquid, however, appear to be inferential rather than based on direct experimental determinations of the viscosity. Thus in one instance,[2] while using *p*-cymene as an adhesive, he found that a series of adhesion measurements between glass and steel gave results which were too low as compared with the results of certain other measurements considered normal. This led him to assume that the layer of *p*-cymene, which was 4 microns in thickness, had been changed by the fields of force of the inclosing solids from a "light spirit" to a "jelly." The molecules of the liquid were supposed to have been oriented and "locked in place by the attraction fields of the solids," the viscosity increasing to at least 200 times its normal value as a result. As expressed in his latest paper,[3] Hardy's final view is to the effect that none of the liquid between two solid surfaces is "free" unless the surfaces are separated by a distance greater than 10μ. No additional experimental data to substantiate this view are given.

Many other investigators have put forth evidence to show that the viscosity of liquids, particularly of lubricating oils, is influenced to a considerable distance by a solid surface. Thus Gilson,[4] Becker,[5] and others have reported that the composition of the metals in a journal bearing influences the coefficient of friction in the régime of complete film lubrication when the shaft and journal are separated by a relatively thick film of lubricant. This is not in accord with the accepted theory of lubrication,[6] and it could be brought about only by a specific effect of the metals on the viscosity of the liquid film. It is difficult to reconcile the conclusions of these investigators with the

[2] W. B. Hardy and Millicent Nottage, Studies in Adhesion, Proc. Roy. Soc. A, **112**, pp. 62–75; 1926.
[3] The Analysis of Commercial Lubricating Oils by Physical Methods, Lubrication Research Tech. Paper No. 1, Dept. Sci. and Indust. Res., London, 66 pp.; 1930.
[4] E. G. Gilson, Lubrication Round-Table Discussion, Ind. Eng. Chem., **20**, pp. 847–848; 1928.
[5] A. E. Becker, Surface Action and Fluid Film Lubrication, Ind. Eng. Chem., **18**, pp. 471–477; 1926.
[6] Mayo D. Hersey, Fundamental Action of Lubricants, Am. Machinist, **70**, pp. 919–921; 1929.

work of Kingsbury,[7] who experimented at high rates of shear with "a slightly tapered plug rotating in a ring, the parts being of hardened steel, closely fitted by grinding. With films as thin as 0.000025 inch (0.6μ) and rates of shear up to 261,000 radians per second, at atmospheric pressure and temperature, there was no indication of slip, and no deviation from the oridnary law of viscosity that could not be attributed to inaccuracy of the fitted surfaces."

Perhaps the most remarkable results to be found in the literature are those on the clogging of capillaries reported by Wilson and Barnard.[8] These authors found that when oil containing a small amount of fatty acid or other polar material was allowed to flow through capillaries as large as 0.3 mm inside diameter, the capillaries gradually clogged and in many instances were closed up completely in a few hours. The mechanism of clogging is pictured as the progressive formation of an immobile layer on the inside of the capillary due to orientation and selective adsorption of the polar components. These results have met with wide acceptance among scientific and technical workers in many countries. They constitute in large measure the foundation for a theory which Karplus [9] has formulated to embrace both the régimes of boundary and complete film lubrication. They are quoted in the masterly treatise of Woog,[10] although Woog discovered that the clogging he observed in some similar experiments of his own was due to the lodging of foreign threadlike filaments in the capillary. Vieweg and Kluge [11] consider the work of Wilson and Barnard to be of such fundamental importance that they have recently republished several of the original diagrams to show the clogging of capillaries with prolonged flow of liquid. Dover [12] repeated the clogging experiments taking great care to reproduce Wilson and Barnard's conditions as closely as possible. She found that the capillaries became clogged, but she obtained "very erratic results." Ormand,[13] Ries,[14] Johansen,[15] and others also indorse the Wilson and Barnard theory of thick-film adsorption.

III. THE CLOGGING OF COARSE CAPILLARIES

In view of the wide acceptance given the above-mentioned experiments on the clogging of capillaries, it was deemed advisable to repeat them before attempting the more difficult task of measuring the flow of liquids through finer capillaries than have been used for this purpose heretofore. At first a viscometer was employed which was purposely of an entirely different design from that of Wilson and Barnard to avoid any inherent faults that may have been present in their apparatus or method. The instrument was so constructed as to bring the different variables under direct control. For example,

[7] Albert Kingsbury, Report of Subcommittee on Lubrication, Mech. Eng. **41**, p. 537; 1919.
[8] R. E. Wilson and D. P. Barnard, Fourth, Measurement of the Property of Oiliness, J. Ind. Eng. Chem., **14**, pp. 683–694; 1922.
[9] Hans Karplus, Der Aufbau der Schmierschicht und die Kolloid-graphitschmierung, Petroleum Zeit., **25**, pp. 375–386; 1929.
[10] Paul Woog, Contribution à L'Étude du Graissage, Delagrave, Paris, 1926.
[11] V. Vieweg and J. Kluge, Ueber Messungen der Schmierfähigkeit von Oelen in Lagern, Archiv. f. das Eisenhüttenwesen, **2**, pp. 1–7, 1929.
[12] M. V. Dover, Lubricating Efficiencies of Oils, Ind. Eng. Chem., **18**, p. 499; 1926.
[13] W. R. Ormandy, Lubrication, Proc. Inst. Mech. Eng., **1**, pp. 291–329; 1927.
[14] E. D. Ries, Relation between Physical Characteristics and Lubricating Values of Petroleum Oils, Ind. Eng. Chem. Analytical Ed., **1**, p. 187; 1929.
[15] E. M. Johansen, Interfacial Tension between Petroleum Products and Water, Ind. Eng. Chem., **16**, pp. 132–135; 1924.

the pressure producing the flow could be varied at will, a constant temperature bath was employed and only a single capillary was investigated at a time. Four capillaries in all were investigated; one of glass, 0.20 mm inside diameter; one of nickeline, 0.25 mm inside diameter; one of platinum, 0.25 mm inside diameter; one of steel, 0.35 mm inside diameter.

Clogging was experienced from the start. In Figure 1 are shown graphs for three typical runs using essentially the same method of plotting as employed by Wilson and Barnard. However, since the pressure producing flow was not constant but was purposely varied

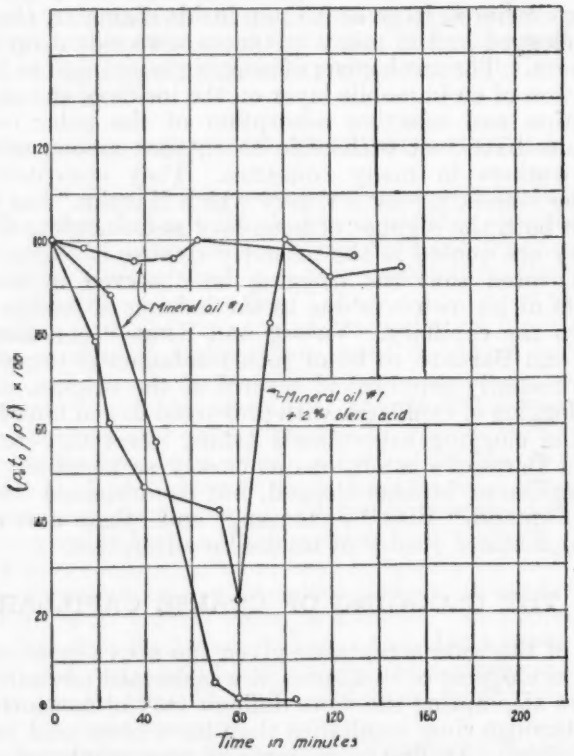

FIGURE 1.—*Flow of inadequately filtered oils through coarse nickeline capillary*

from time to time to test the proportionality of rate to pressure difference, it is the $p\,t$ value instead of the rate of discharge which should here remain constant for a nonclogging oil,[16] that is, the ratio $p_o t_o/pt$ should always be unity for nonclogging oils, p_o being the initial pressure producing flow, t_o the initial time for unit discharge, and p and t the corresponding values at any subsequent time.

As in the tests of Dover, the most characteristic feature of these graphs is their erratic appearance. Wilson and Barnard and Dover used only a 200-mesh sieve (see fig. 2) for filtering the oils they tested. In the present investigation all liquids, whether for test or for rinsing

[16] Emil Hatschek, The Viscosity of Liquids, D. Van Nostrand Co., 1928.

the apparatus, were filtered through an asbestos or paper filter, but still without consistent results. To prevent contamination from the atmosphere and to minimize the number of fibers which might be detached from the under side of the filter, a pellet of loosely packed clean cotton wool was placed directly over the entrance to the capillary where it was allowed to remain during test, no other filtering of the liquid being employed. The rate of flow was then found to be not only steady with time at a given pressure difference, but also directly proportional to the pressure producing the flow. Repeated tests with various oils and capillaries served only to confirm the evidence that a filtering device as simple as a cotton pellet was sufficient in all cases to give consistent and reproducible results with capillaries as large as those listed above.

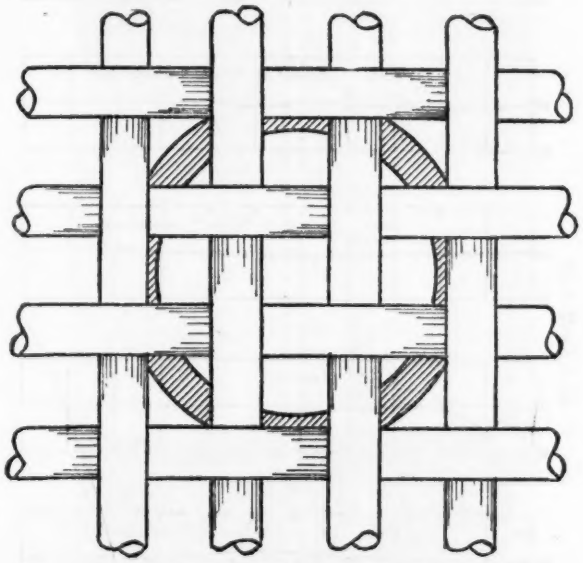

FIGURE 2.—*Magnified sketch of capillary 0.3 mm inside diameter beneath 200-mesh sieve*

In all, 18 complete tests were made before adopting the expedient of filtering inside the instrument. These embraced tests made in all four capillaries with several different kinds of oil, both fatty and mineral. In 12 of these tests clogging took place to the extent of retarding the rate of flow 20 per cent or more. After adopting the cotton-wool method of filtering, 10 runs were made using the same oils and capillaries. None of the 10 showed clogging sufficient to slow down the rate of flow by as much as 10 per cent, and only 1 run showed a decrease in the rate greater that 5 per cent. Figure 3 shows typical graphs for test data on three of the capillaries using the improved method of filtering. On the thick adsorbed-film theory all the oils used here should clog the capillaries rapidly.

The four capillaries were next mounted in an apparatus exactly similar to that of Wilson and Barnard as shown in Figure 4. Figure 5 shows curves for typical runs made on an oil containing 1.2 per cent stearic acid using Wilson and Barnard's method of test. Figure 6

shows tests on the same oil under identical circumstances except that a loose layer of cotton was used to cover the capillaries. These tests were made without temperature control, and the variations in rate for the tests of Figure 6 are well within the errors to be expected. To demonstrate that the cotton had no other effect than to filter out foreign particles, a great mass of it was saturated with oil and allowed to stand for 24 hours. Enough oil for test was then gently expressed and tested by Wilson and Barnard's method. Clogging was as pronounced as in any previous test, but when the capillaries were cleaned

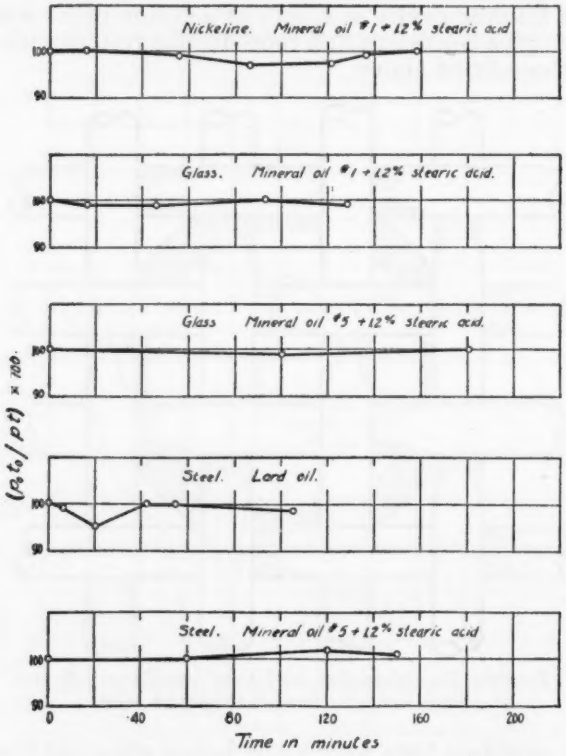

FIGURE 3.—*Flow of oils through coarse capillaries, improved filtering*

and covered loosely with some of the same cotton the rate of flow was steady at its initial value for several hours. The results obtained up to this point seem to show conclusively that the clogging of capillaries observed by Wilson and Barnard could be attributed mainly, if not entirely, to foreign matter in the oils they used.

IV. FLOW TESTS OF LIQUIDS IN FINE CAPILLARIES

1. DESCRIPTION OF INSTRUMENT AND MANNER OF OPERATION

It is obvious that tests must be performed under better experimental conditions than those just described, and that more searching criteria must be applied to the tests if it is desired to gain a quantita-

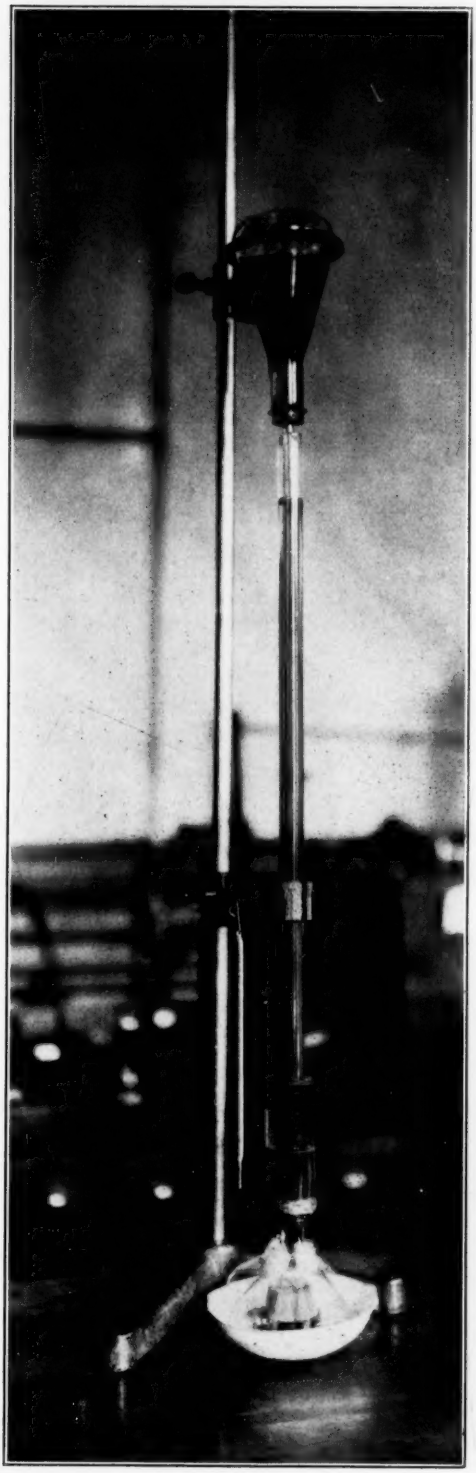

FIGURE 4.—*Apparatus similar to that of Wilson and Barnard*

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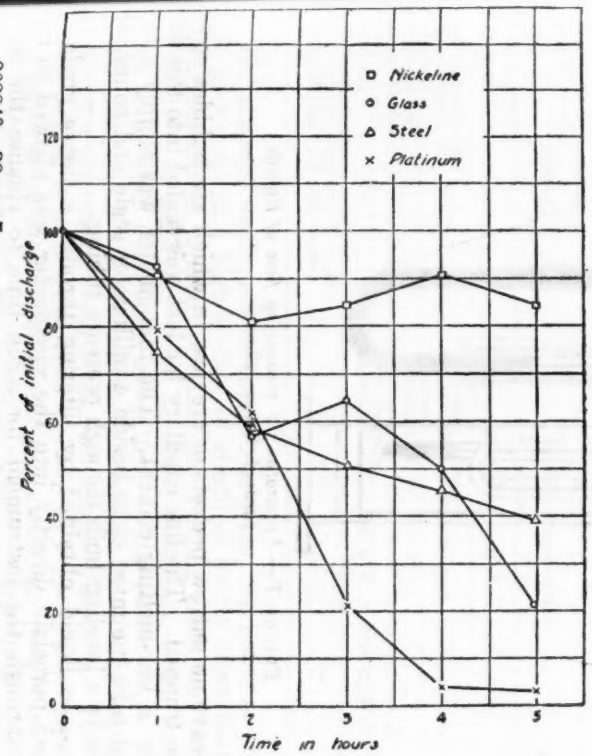

FIGURE 5.—*Clogging of capillaries in Wilson and Barnard apparatus*

Mineral oil No. 1+1.2 per cent stearic acid

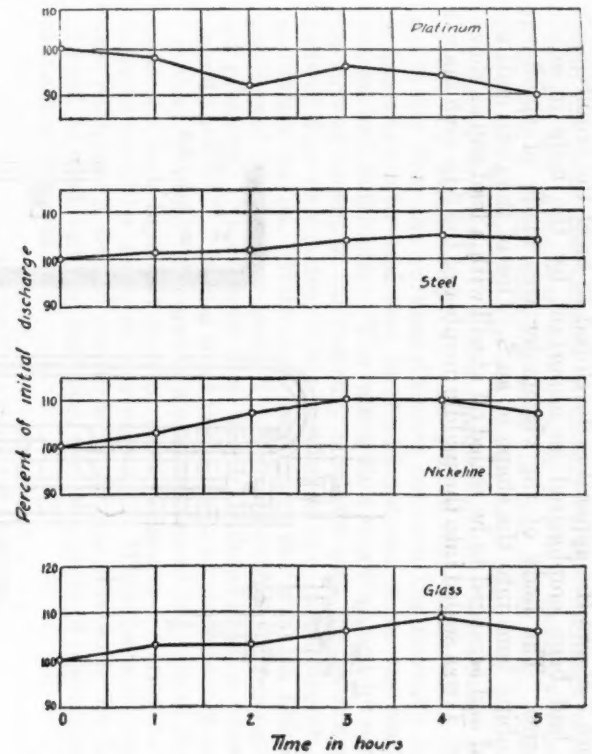

FIGURE 6.—*Same apparatus and oil as Figure 5 improved filtering*

tive idea as to the thickness of the stagnant layer adjacent to the walls of the capillary.

Figure 7 shows the apparatus developed to meet the requirements which had been emphasized as important by the tests in coarse capillaries. The body of the viscometer was made of small-bore glass tubing bent into the shape of an S. One of the open ends was tapered and arranged to be sealed off at will with a lead cap as shown. A short T was sealed into the middle member of the S in such manner

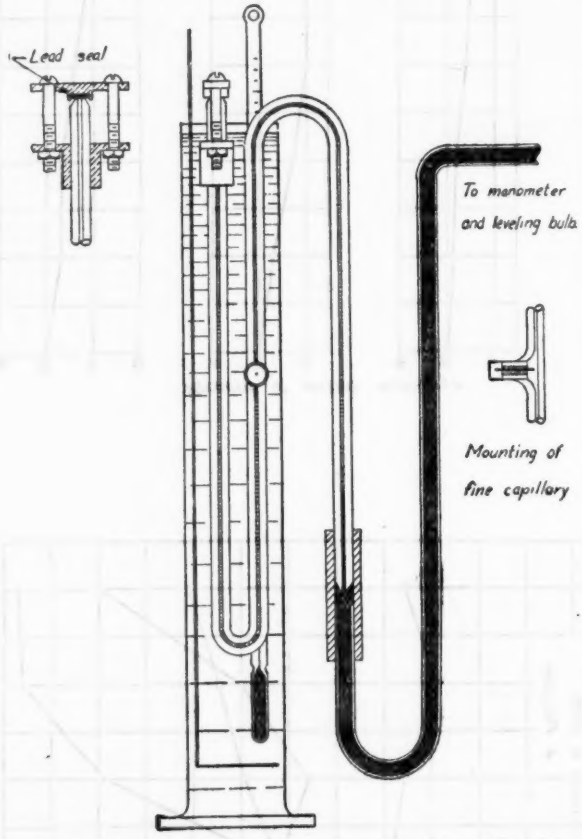

FIGURE 7.—*Apparatus for measuring flow of liquids through fine capillaries*

as to leave no narrow pockets or crevices in which air bubbles could become trapped. The fine capillary for test was sealed into this side tube by a low-melting cement. The manometer was simply a tall vertical tube mounted close beside a millimeter scale and connected directly to a leveling bulb through pressure tubing.

Dust-free liquid obtained by filtering through a dense grade of unglazed porcelain directly into the viscometer was allowed to run freely through the instrument for some time to cleanse the walls thoroughly of any loose particles of dust. Then, with the instrument completely full of test liquid, the cap was screwed into place and the

viscometer was connected with the pressure system in such manner as to place the test liquid in direct contact with the mercury. To avoid an interfacial tension correction at the discharge end of the capillary the latter was immersed in a small auxiliary thermostat filled with a liquid miscible with the one under test. This small thermostat, along with the viscometer, was placed in a larger bath not shown in Figure 7, which maintained the temperature constant at 30° C. within 0.01° C. To obtain the uncorrected pressure producing flow the vertical distance between the mercury meniscus in the viscometer and that in the manometer tube was read to the nearest half millimeter. The rate of flow was obtained by measuring the rate of ascent of the mercury meniscus into the calibrated right limb of the viscometer, using a miscroscope cathetometer reading accurately to 5μ. With few exceptions the error in reading the position of the mercury menisci was not in excess of 1 per cent of the net pressure. No rates of flow were calculated from a time of less than 40 seconds or from a total vertical rise of the mercury meniscus less than 0.5 mm. Accurate determinations of the rate of flow were made for each liquid at four or more pressures covering as wide a range as could be managed conveniently. When tests on one liquid were complete a second dust-free liquid miscible with the first was allowed to wash out the first one, and the cycle of operations given above was repeated.

2. PURIFICATION OF LIQUIDS

The essential information for the liquids used is given in Table 1.

TABLE 1.—*Liquids used in viscosity tests*

Liquid	Criterion of purity	Viscosity, 30° C. poises
Benzene	Timmermans'; M. P. 5.493°C	0.00574
Do	Baker's C. P	.00575
Conductivity water	Superpure, pH=6.7	.00801
White mineral oil	Special treatment with sodium	.151
Oleic acid	Eastman's	.256
n-caprylic acid	Eastman's; M. P. 14° to 15° C	.0463
n-butyl alcohol	Eastman's; B. P. 116° to 118° C	.0230
Ethyl alcohol	Absolute grade	.0100
p-cymene	Eastman's; terpene-free, B. P. 176.5° to 177.5° C	.00752
Kerosene		.0188
White oil plus 1 per cent oleic acid		.152
White oil plus 1 per cent *m*-cresol		.146

No attempt was made to obtain the acids, the butyl alcohol, and the *p*-cymene in a higher state of chemical purity than that of the best commercial product obtainable. Putting aside the very great difficulty [17] of purifying some of these materials, there would still seem to be little purpose in using them in the purest state, since the polar compounds are preferentially adsorbed on a solid surface from a mixture containing both polar and nonpolar bodies. This preferential action is so marked that as little as 2 per cent of stearic acid in a mineral oil may be as effective in reducing friction as the pure acid. Moreover, the impurities present in compounds of this type

[17] Arthur Lapworth, Leonore K. Pearson, and Edward N. Mottram, The Preparation and Properties of Purified Oleic Acid, Biochem. J., **19**, pp. 7-18; 1925.

are usually other polar compounds which are not likely to diminish the thickness of the adsorbed layer or lessen in any other way the change in viscosity which may take place due to contact with a solid surface.

This same phenomenon, the preferential adsorption of the polar bodies, imposes the requirement that the nonpolar liquids shall be scrupulously pure and free from polar material. The ultimate standard or reference liquid which was chosen to fulfill this condition was pure benzene. As auxiliary reference liquids not likely to contain molecules with a "loaded end," conductivity water and a specially prepared white mineral oil were used. The pure benzene was obtained from the laboratory of Prof. J. Timmermans, of the University of Brussels. This benzene is recommended by the International Bureau of Physical Chemical Standards as possessing the highest possible purity obtainable.[18] The conductivity water was prepared in the laboratory of Dr. S. F. Acree, of the National Bureau of Standards, in the special stills developed largely under his direction.

This water was free from sprayed-over impurities and from carbon dioxide. It gave a pH of 6.7 when tested with a brom-thymol blue indicator adjusted to give the same pH.[19] The specially prepared mineral oil was selected as answering, about as well as anything to be had, the need for a pure nonpolar compound or mixture of compounds in the paraffin series. The white oils as purchased are generally recognized as being free from polar compounds. However, in order to be reassured on this point the oil was allowed to stand for several days over a large amount of freshly cut sodium. It was agitated frequently during this period and the presumption is that any bodies likely to be selectively adsorbed by platinum or glass were similarly adsorbed by the much more active sodium and removed. The oil was then filtered and washed with warm distilled water until, when a sample of it was shaken with phenolphthalein, neither the oil nor the water layer showed any color after standing several hours. It was then dried for some days over C. P. calcium chloride, filtered and carefully stoppered.

The porcelain filters which were used to remove dust from the liquids were, when new, invariably found to impart an alkaline reaction to water filtered through them. They were accordingly boiled for some time in dilute acetic acid and then rinsed repeatedly in distilled water until a sample of conductivity water gave the same pH after filtering as before, namely, 6.7. The filters were then thoroughly dried and stored in a clean cabinet until needed.

With the exception of the value for conductivity water the viscosities quoted in Table 1 were determined in the viscometry laboratory of the National Bureau of Standards by F. G. Bitner. A Bingham viscometer was used which had been calibrated with distilled water, taking as the viscosity of the latter the value recommended by Professor Bingham [20] and used at the National Bureau of Standards. The value quoted by Professor Timmermans, for the viscosity of his benzene is 1.4 per cent lower than the value given in Table 1. Tim-

[18] J. Timmermans and F. Martin, Étude de Vingt Hydrocarbures et Dérivés Halogénés, J. Chim. Phys., **23**, pp. 747–787; 1926. See also same volume, pp. 733–746.

[19] S. F. Acree and Edna H. Fawcett, The Problem of Dilution in Colorimetric H-Ion Measurements, J. Bact., **17**, pp. 163–204, 1929. Also see Fawcett and Acree under the same title in Ind. Eng. Chem., Analy. Ed., **2**, pp. 78–85; 1930.

[20] Eugene C. Bingham and Richard F. Jackson, Standard Substances for the Calibration of Viscometers, B. S. Sci. Paper No. 298. B. S. Bulletin, **14**, pp. 59–86; 1918–19.

mermans and Martin used an Ostwald viscometer which also had been calibrated with water, but they chose for the viscosity of the latter the mean of the values given in Landolt-Börnstein. No details of the viscosity determinations are given and it is believed that the values given in Table 1 are more reliable than that determined by Timmermans and Martin.

3. THE VISCOSITY EQUATION; CORRECTIONS TO BE APPLIED

Bingham,[21] Hatschek,[22] and others have treated the theory of viscous flow of a liquid through a capillary tube so thoroughly that no discussion of the general principles involved need be given here. The complete equation may be written

$$\eta = \frac{\pi P R^4 t}{8(L+\lambda)Q} - \frac{m Q d}{8\pi(L+\lambda)t} \tag{1}$$

where

η = viscosity of liquid in poises.
P = pressure producing the flow in dynes/cm^2
R = radius of capillary in centimeters.
L = length of capillary in centimeters.
Q = volume of liquid in cm^3 discharged in t seconds.
d = density of liquid in g/cm^3.
m = coefficient of kinetic energy correction.

and

λ = Couette or end correction.

The correct values to be used for m and λ have been the subject of much controversy. This does not concern us here, however, since both λ and the last term of equation (1) are negligible for the conditions which prevailed in the present investigation. The extreme values quoted in the literature for λ are of the order of 1 or 2 diameters, with a strong probability that it is less than a single diameter. In the present investigation this correction was largest in the case of capillary D, of platinum, with a length of 1.35 cm and a diameter of approximately 0.0027 cm. The correction was, therefore, less than 0.5 per cent, which is less than the error from other sources. The last term of equation (1) had its maximum value for the tests on water in the capillary just described. Accepting the value of 1.12 usually given for m, the last term was in the worst case only a hundredth of 1 per cent as large as the preceding term. Equation (1) then reduces at once to the form

$$\eta = \frac{\pi P R^4 t}{8 L Q} \tag{2}$$

which is Poisuelle's law. For our present purpose it will be more convenient to write this equation in the form

$$R^4 = \frac{8 L \eta q}{\pi P} \tag{3}$$

where $q = Q/t$, the rate of discharge in cm^3 per second.

[21] E. C. Bingham, Fluidity and Plasticity, McGraw-Hill; 1922.
[22] Emil Hatschek, The Viscosity of Liquids, D. Van Nostrand Co.; 1928.

In practically all forms of efflux viscometer the apparent volume of liquid which has passed in a given time must be multiplied by a drainage factor to correct for the liquid which adheres to the walls of the measuring bulb. In the tables and graphs to follow, the rate of flow, q, has been calculated on the assumption that the mercury as it rose in the measuring tube displaced all the test liquid and filled the tube completely. As seen through the microscope, this condition seemed to be realized, but it is obvious that such could not actually have been the case. Hickman,[23] however, has shown that a mercury drop placed on an oily surface soon squeezes out all the oil beneath it except a layer approaching molecular dimensions in thickness. The following test was made to determine the approximate thickness of the layer which adhered to the measuring tube of the viscometer after the mercury had displaced the oil.

A thin-walled glass tube was cleaned, dried, and accurately weighed. It was connected to the pressure system of the viscosity apparatus in place of the viscometer and was held in a vertical position. It was filled with oleic acid, and the leveling bulb was slowly raised to make the mercury pass upward into the tube at about the same vertical rate as was used, on the average, in the viscosity tests on oleic acid. The acid was thus displaced by mercury under conditions closely similar to those prevailing in the actual test. When the tube was completely filled with mercury it was dismounted, emptied of mercury, and wiped clean on the outside. It was weighed again, the difference between weighings representing the amount of oleic acid adhering to the inside walls. When the volume of this acid was divided by the total inside area of the tube the thickness of the layer was given as 11×10^{-5} cm. Assuming the same thickness of layer to adhere to the walls of the viscometer the volume of acid not displaced by the mercury in a test would be less than 1 per cent of the nominal volume of flow. It would be still less than this for the other liquids used. The correction was, therefore, considered negligible.

A correction of more importance is that which must be applied to the observed pressure to account for the capillary depression of the mercury meniscus in the measuring tube of the viscometer. This correction is hereafter called c, and it was determined separately for each liquid in the following manner: A U-tube was made in which one leg had closely the same inside diameter as the manometer and the other the same inside diameter as the measuring tube of the viscometer. The piece was mounted upright open to the atmosphere at both ends, mercury and test liquid being in contact in the small leg and clean mercury alone standing in the large leg. A little more mercury was then poured into the large leg to make the level in both sides rise. The vertical distance between the two mercury levels was then accurately measured with a cathetometer. This was repeated several times, the average vertical distance between the mercury surfaces for a given liquid being taken as the c value. This value was found to be independent of the rate of rise of the mercury levels from zero rate up to the maximum used in tests, which was less than a centimeter a minute.

The head of mercury effective in producing flow is here called p and is equal to $(m-h-c)$ where m is the vertical distance between the

[23] K. C. D. Hickman, The Mercury Meniscus, J. Opt. Soc. Am. and Rev. Sci. Inst. **18**, pp. 190-212, 1929.

mercury level in the instrument and that in the manometer tube and h is the correction for the head of liquid in the thermostat against which the test liquid discharged. The value of h was always something less than a centimeter of mercury and changed somewhat during the tests on a given liquid as the mercury rose in the measuring tube. The value of P in equations (1), (2), and (3) is the driving pressure in dynes per cm^2. It was obtained by multiplying p by the density of mercury at the average temperature of the room, taken as 25° C., and by the acceleration of gravity. The change in p during a test was small, and the difference between its effective value and the mean of its final and initial values has been disregarded. The final form of equation used in calculating the effective radius, with all the numerical values inserted which do not depend on either the liquid or the capillary, is

$$R^4 = \frac{8L\eta}{3.1416 \times 981 \times 13.53} (q/p) \qquad (4)$$

In the diagrams which follow q in cm^3/sec. has been plotted against p in cm of mercury, retaining the latter as a pressure unit in order to avoid unnecessary multiplications. It may be well to note that the ratio q/p is merely the slope of the flow-pressure graph.

4. EXPERIMENTAL RESULTS AND THEIR INTERPRETATION

(a) TESTS IN GLASS CAPILLARIES A, B, AND C

Tests in these capillaries were performed while experimenting with various methods for obtaining dust-free liquids and while developing the technique of test. The results will not be discussed in detail, but one or two items of significance will be mentioned. It was discovered, for instance, that air must be rigorously excluded from the viscometer during test or a greatly exaggerated apparent rate of flow would be obtained, due to the solvent action of the test liquid on the contained air at pressures higher than atmospheric. Several methods of cleaning a fine glass capillary which had become clogged were tried, but none of them proved successful. Whenever a glass capillary clogged up, therefore, it was abandoned for another.

To determine how closely the flow through the capillaries conformed to the simple viscosity equation, the following criteria have been applied to the results of tests made in these capillaries, as well as to all that follow.

1. Is the radius of the capillary as calculated from equation (4) the same for different chemical compounds?

2. Is the rate of flow steady with time for constant pressure difference?

3. Is the rate proportional to the pressure producing the flow?

The significance of these criteria will be discussed more fully after the experimental results for capillary D have been given.

When applied to the tests in capillaries A, B, and C, these criteria gave no indication of an adsorbed layer of appreciable thickness for any of the liquids tested. In some instances the liquid ran continuously through the capillary for four hours without any evidence of clogging. The points on the flow-pressure graphs were somewhat scattered in the earlier tests, but there was no systematic departure

from linearity. Moreover, in these tests, as in all that follow, the results were independent of the order in which the points were taken. In some instances the first datum point was taken at the lowest pressure used for that graph, the next point at the highest pressure and the others at intermediate pressures. Other sequences were used for other liquids.

Two liquids were tested in capillary A: (1) A mineral oil plus 2 per cent oleic acid, and (2) U. S. P. oleic acid. The calculated values of the radius differed by 0.2μ. Conductivity water and butyl alcohol were tested in capillary B, the viscometer receiving a quick rinse with filtered ethyl alcohol in between. The calculated values of the radius differed by 0.4μ. In capillary C white mineral oil, oleic acid, benzene, and butyl alcohol were tested in the order named, with a maximum deviation of 0.26μ from the average calculated radius.

(b) TESTS IN CAPILLARY D, PLATINUM

Platinum was found to possess the advantage over glass that a given capillary, after clogging, could be removed from the instrument, cleaned by flaming just to redness, and used again. On the other hand, the platinum tubes were no doubt rougher on the inside than the glass capillaries. In general, clogging was found to be more frequent with platinum than with glass. This was attributed to roughness, the belief being that such filaments as did get into the viscometer found anchorage more readily along the serrated walls of the platinum tube than along the molecularly smooth walls of the glass ones.

The liquids listed in Table 2 were tested in capillary D. Although the capillary had not clogged, it was removed and gently flamed between the two check runs with white mineral oil. It clogged when the first attempt was made to test butyl alcohol, and it was, therefore, flamed before the test on this liquid which is reported in the table. It was flamed a third time before the test on conductivity water. The flow-pressure graphs are shown in Figure 8.

TABLE 2.—*Summary of tests in capillary D*

[Length, 1.350 cm]

Test liquid	Approximate total duration of test	Calculated radius
	Minutes	μ
White mineral oil	60	[1] 13.53
Do	60	[1] 13.53
Kerosene	50	13.60
Oleic acid	120	13.60
Butyl alcohol	40	13.53
Conductivity water	30	13.60

[1] A single graph was used to average both sets of data for this oil.

Average calculated radius, 13.57μ.
Maximum deviation, 0.04μ.

The significance of the three criteria given above may be considered to advantage at this point. The fundamental assumption underlying the derivation of equation (1) is that the linear velocity of the liquid passing through a small tube is zero only at the mathemetical wall

of the capillary. The velocity of a layer any distance, r, from the axis of the tube is given by the expression,

$$v = \frac{P}{4L\eta}(R^2 - r^2) \tag{5}$$

which is the equation of a parabola, and shows the manner of variation of the linear velocity of the liquid along the radius of the tube. If, due to adsorption, the laminae at a finite distance from the walls

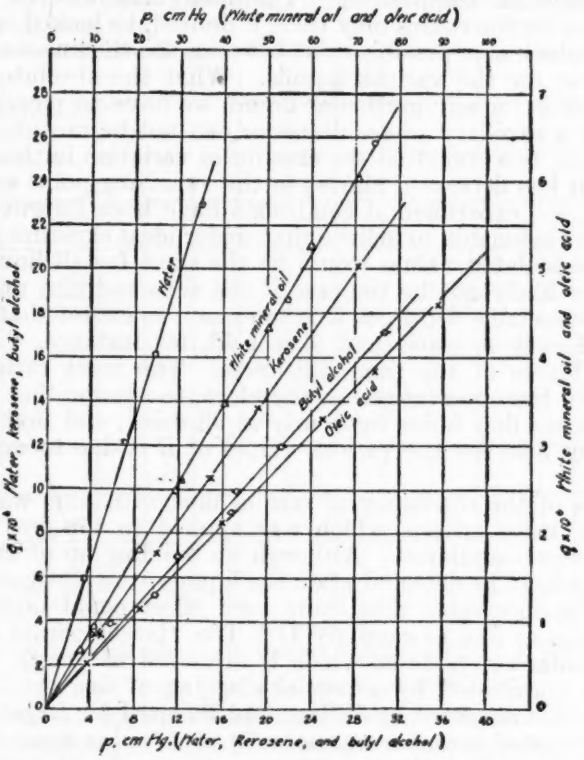
p. cm Hg (White mineral oil and oleic acid)
q x 10⁶ Water, kerosene, butyl alcohol
q x 10⁶ White mineral oil and oleic acid
Water
White mineral oil
Kerosene
Butyl alcohol
Oleic acid
p. cm Hg. (Water, Kerosene, and butyl alcohol)

FIGURE 8.—*Flow-pressure graphs for dust-free liquids in capillary D, platinum*

are held immobile or are retarded in such manner as to produce a distortion of the normal parabolic arc, this retardation or distortion will constitute a virtual reduction of the radius. Since the rate of flow is proportional to the fourth power of the radius a small reduction will be reflected in a relatively large decrease in the rate of flow. If a direct measurement of the diameter is possible, we are able at once to evaluate the magnitude of the reduction for any given liquid by comparing the measured diameter with the effective diameter as calculated from flow data by the viscosity equation. This requires, of course, that the viscosity of the liquid shall have been previously determined in a tube so large as to leave no question but that the reduction or constriction of the diameter due to adsorption was negligible.

If, as in the present case, the diameter of the capillary can not be readily determined by direct measurement we may still hope to obtain valuable information by making appropriate tests and calculations. We can, for instance, calculate the effective radius for each of several liquids of different chemical compositions and compare the different values so found. If the adsorbed layer differs appreciably in thickness for different liquids we should by this means be able to arrange the liquids in the order of increasing thickness of adsorbed layer and estimate, at least roughly, how the thickness varies with the chemical composition. The differences between the calculated values for the radius may then, if desired, be looked upon as the difference which may possibly exist between the thicknesses of the adsorbed layer for the various liquids. What the absolute thickness of this layer is for any particular liquid, we have no means of determining for a capillary whose diameter can not be meaured directly. It is striking, however, that the amount of variation in the calculated values of R has decreased almost to the vanishing point as the technique and the experimental conditions have been improved, and it seems only reasonable to believe that under ideal experimental conditions the calculated values would be the same for all liquids. This would very likely not be the case if the adsorbed film on the walls were of appreciable depth, as it is too much to expect that liquids as widely different as water and oleic acid, for instance, should have adsorbed layers of the same thickness. The most rational interpretation of the observations is, therefore, to assume that the law of simple viscous flow holds rigorously in all cases, and that the whole discrepancy between the various values of R is due to experimental error.

The test of the constancy of rate of flow with time was the only one of the three criteria which was applied to the flow of liquids through coarse capillaries. Although no building up of an adsorbed layer could there be detected when the liquids were adequately filtered it is not inconceivable that some such effect could manifest itself in capillaries as fine as capillary D. The "latent period of orientation" of polar compounds, which is discussed at length by Hardy, should be manifested by a partial clogging of fine capillaries very similar to that observed by Wilson and Barnard for larger ones. As already indicated, clogging was actually observed in some of the tests attempted in capillary D, but this was always of such a nature as to leave no room for doubt that it was produced by foreign particles. Progressive decrease in the pt value was always accompanied by the same erratic behavior as characterized the clogging of coarse capillaries. For such tests the flow-pressure graphs were not linear and the calculated radii for all the points on the graph were less than for liquids which did not clog. When clogging was experienced in a first test of any particular liquid, a second attempt under more rigorous experimental conditions almost invariably proved successful in giving a run free from clogging. The middle column of Table 2 shows, for the various materials, the approximate period during which the liquids were actually flowing through the capillary. Over this period the pt value was constant within the experimental error of the tests.

If there is a deep, stagnant layer next to the walls, its thickness, and, therefore, also the effective radius of the capillary, are very probably functions of the rate of flow and hence of the pressure dif-

ference producing flow. Very close to the walls the film must be held entirely rigid and immobile, but at a little distance away we can suppose it to be less stable, due to the decreasing strength of the fields of force. Those portions of the film at some distance from the walls should then be swept along by high velocities of flow, but it is possible that they would reform and remain immobile when the velocity is decreased. We might reasonably expect to find, therefore, that the rate of flow is not a linear function of pressure unless the film is of an entirely insensible thickness. The flow-pressure graphs of Figure 8 pass through the origin and leave little to be desired in the way of linearity.

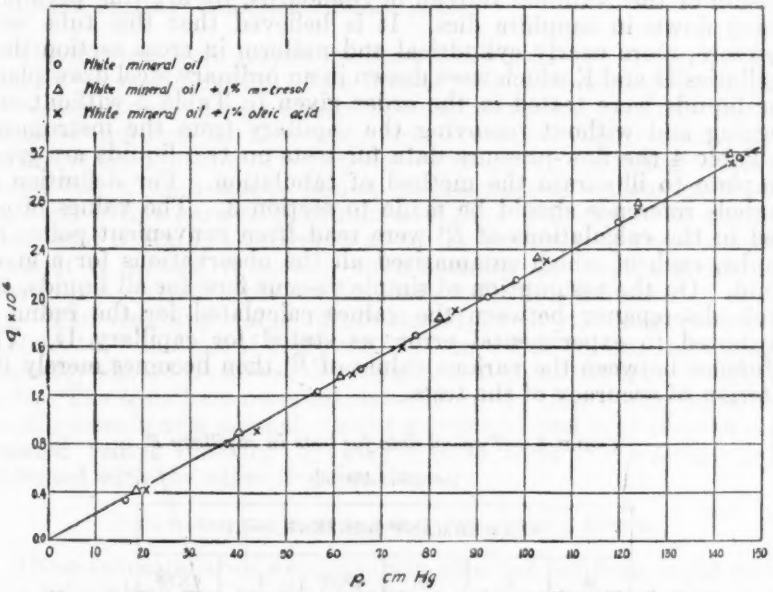

FIGURE 9.—*Flow-pressure graphs for tests in capillary E, platinum*

(c) TESTS IN CAPILLARY E, PLATINUM

Figure 9 shows that the same conclusions as drawn from the tests on pure or nearly pure liquids in capillary D, apply equally well to tests on solutions of polar compounds in a nonpolar oil. Wilson found pronounced clogging of coarse capillaries with oils containing *p*-cresol. Merely because it was easily available, *m*-cresol was used here instead. The line in Figure 9 has been drawn to average the tests with white mineral oil; the graphs averaging the other two sets of points have been omitted to avoid confusion.

TABLE 3.—*Summary of tests in capillary E*

[Length, 1.480 cm]

Test liquid	Approximate total duration of test	Calculated radius
	Minutes	*μ*
White mineral oil	60	9.85
White mineral oil plus 1 per cent *m*-cresol	60	9.81
White mineral oil plus 1 per cent oleic acid	60	9.86

Average calculated radius 9.84μ.
Maximum deviation 0.03μ.

The liquids were tested in the order named in Table 3 and without removing the capillary for cleaning. To be assured that plenty of the essential "film forming constituents" remained in the filtered oil the acidity of the sample containing oleic acid was determined before and after filtering.

	Per cent by weight
Oleic acid in unfiltered sample	1.0
Oleic acid in filtered sample	.92

(d) FINAL TESTS IN PLATINUM, CAPILLARY F

This capillary was prepared by Dr. L. Jordan, of the metallurgy division of the National Bureau of Standards, by drawing platinum tubing down in sapphire dies. It is believed that this tube was, therefore, more nearly cylindrical and uniform in cross section than capillaries D and E which were drawn in an ordinary steel draw plate. The liquids were tested in the order given in Table 5 without any clogging and without removing the capillary from the instrument. In Table 4 the flow-pressure data for tests on two liquids are given complete to illustrate the method of tabulation. For definition of symbols reference should be made to section 3. The values of q/p used in the calculations of R^4 were read from convenient points on graphs, each of which summarized all the observations for a given liquid. On the assumption of simple viscous flow for all liquids, the whole discrepancy between the values calculated for the radius is attributed to experimental error, as stated for capillary D. The difference between the various values of R^4 then becomes merely the criterion of accuracy of the tests.

TABLE 4.—*Typical data for tests in capillary F*

[Length, 1.480 cm]

TIMMERMANS' BENZENE, $c=1.7$					
m	h	p	$Q\times10^6$	t	$q\times10^6$
16.60	0.65	14.3	5.86	93.0	6.30
28.05	.55	25.8	15.4	125.0	12.3
40.40	.50	38.2	15.4	87.2	17.7
19.75	.35	17.7	8.40	105.0	8.00
31.40	.30	29.4	14.0	101.2	13.8
$R^4=\frac{8\times1.48\times0.00574\times17\times10^{-6}}{3.1416\times981\times13.53\times36.7}=7,569\times10^{-16}$					
$R=9.325\mu$					
n=CAPRYLIC ACID, $c=1.6$					
54.60	0.60	52.4	4.89	159.4	3.07
44.15	.55	42.0	3.90	162.8	2.39
33.65	.55	31.5	4.72	257.8	1.83
23.30	.50	21.2	3.73	298.0	1.25
13.05	.45	11.0	1.87	289.0	0.647
64.60	.40	62.6	3.79	107.6	3.52
$R^4=7,586\times10^{-16}$ $\quad R=9.333\mu$					

TABLE 5.—*Summary of tests in capillary F*

Test liquid	Approximate duration	R^4, calculated	R, calculated
	Minutes	$\times 10^{16}$	μ
Timmermans' benzene	20	7,569	9,325
Baker's benzene	30	7,586	9,333
Oleic acid	60	7,656	9.354
n-caprylic acid	40	7,586	9.333
p-cymene	30	7,647	9.352
White mineral oil	60	7,735	9.378

Average R^4, calculated, $7{,}633\times10^{-16}$; maximum deviation 1.4 per cent
Average R, calculated, 9.349μ; maximum deviation 0.029μ.

The flow-pressure graphs are shown in Figure 10. Only two items call for special mention. The first is that the ordinary C. P. grade of benzene gave a graph almost identical with that resulting from the benzene purified so rigorously by Professor Timmermans. The second is the behavior of *p*-cymene. This liquid, according to Hardy's tests, has a zero latent period of orientation. Accordingly, if it behaves with regard to platinum as it does with regard to glass and steel, and if Hardy's inference as to the influence of these materials upon it is correct, it should, upon entering the capillary, instantly build up a jellylike layer on the inside walls to a thickness of at least 2μ. The resulting value of R^4 should be in the neighborhood of $2{,}500\times10^{-16}$ instead of $7{,}600\times10^{-16}$. In other words, the apparent viscosity should be about three times as high as the true viscosity in bulk. The tests here reported show, however, that the liquid behaves in all respects as a normal viscous substance, and that it gives a calculated radius differing by only 0.003μ from the average radius obtained with the other five liquids.

(e) FINAL TESTS IN GLASS CAPILLARIES G AND H.

These two capillaries were cut from adjacent positions in the middle of a tube which was nearly uniform in cross section and about 4 feet in length. They were, therefore, expected to be of essentially the same radius. Tables 6 and 7 show a summary of the tests, the data for which are plotted in Figures 11 and 12.

TABLE 6.—*Summary of tests in capillary G*

[Length, 1.270 cm]

Test liquid	Approximate duration	R^4, calculated	R, calculated
	Minutes	$\times 10^{16}$	μ
Timmermans' benzene	60	968.9	5.579
p-cymene	60	966.5	5.576
n-caprylic acid	120	991.2	5.611

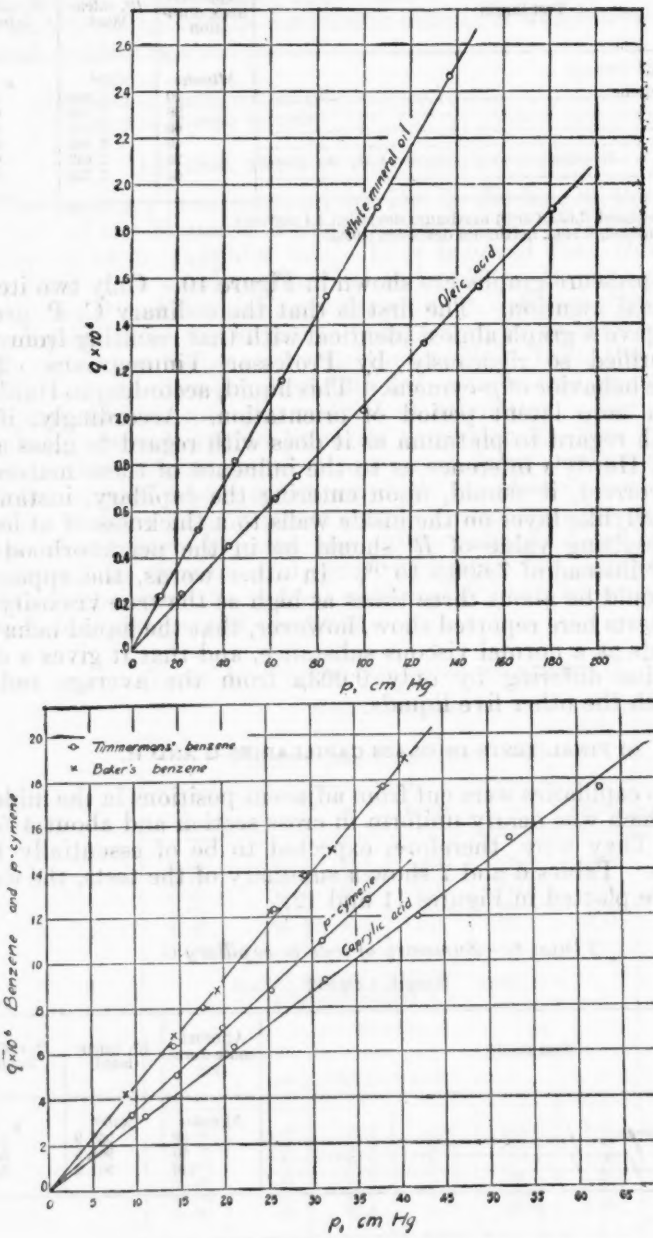

FIGURE 10.—*Final tests in platinum, capillary F*

TABLE 7.—*Summary of tests in capillary H*

[Length, 1.249 cm]

Test liquid	Approximate duration	R^4 calculated	R, calculated
	Minutes	$\times 10^{16}$	μ
Conductivity water	60	962.6	5.570
Ethyl alcohol	60	981.0	5.596
n-caprylic acid	120	983.8	5.601

Average R^4, calculated, capillaries G and H, 975.8×10^{-16}.
Maximum deviation, 1.6 per cent.
Average R, calculated, capillaries G and H, 5.589μ.
Maximum deviation, 0.022μ.

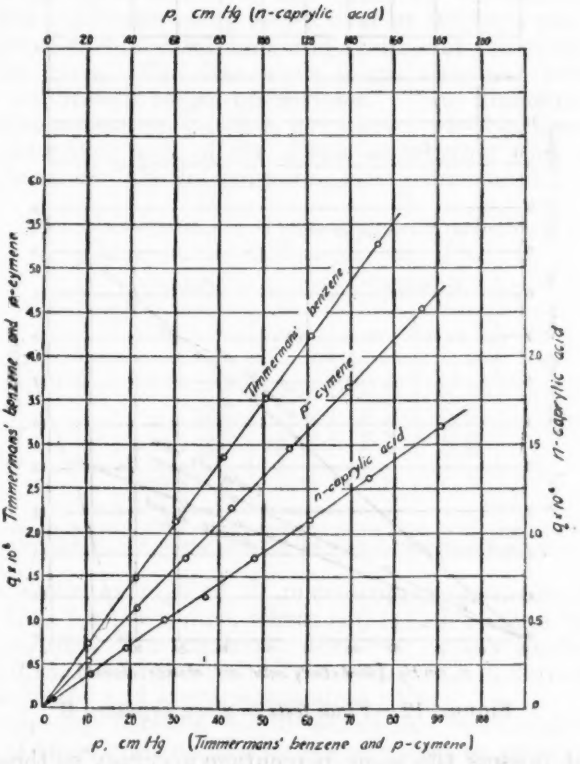
p, cm Hg (n-caprylic acid)
q x 10⁴ Timmermans' benzene and p-cymene
q x 10⁴ n-caprylic acid
Timmermans' benzene
p-cymene
n-caprylic acid
p, cm Hg (Timmermans' benzene and p-cymene)

FIGURE 11.—*Final tests in glass, capillary G*

Glass was one of the materials, which, in Hardy's experiments, appeared to exercise a profound influence on the viscosity of *p*-cymene to a distance of 2μ. The tests here reported show no effect at distances of the order of 0.02μ.

It is usually stated that the time required for the polar molecules to reach their maximum degree of orientation is greatly decreased by vigorous agitation or shear. For polar liquids passing rapidly through a capillary tube the conditions should then be particularly favorable for the prompt formation of the rigid oriented film on the walls. The tests heretofore discussed in this paper constitute strong evidence

that no such rigid film exists of a greater thickness than 0.02μ. There remains the possibility that an effect is present which is masked rather than accentuated by the shearing of the layers of liquid past each other through the capillary. This effect should manifest itself to best advantage in a test made at a low rate of shear after the liquid had been allowed to remain undistrubed for a long period of time so as to allow the walls of the capillary to produce maximum orientation upon the inclosed molecules.

The data for the last and lowest point shown on the graph for *n*-caprylic acid on Figure 11 were obtained under such circumstances,

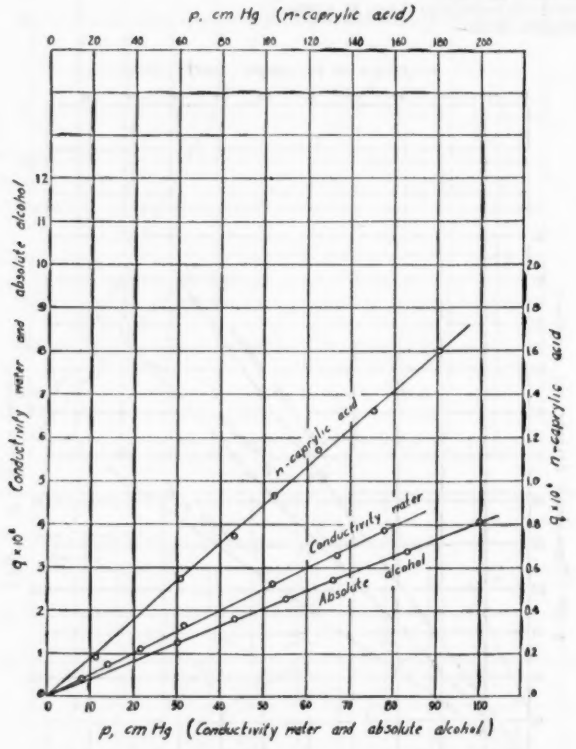
p, cm Hg (n-caprylic acid)
0 20 40 60 80 100 120 140 160 180 200
q×10⁴ Conductivity water and absolute alcohol
12 11 10 9 8 7 6 5 4 3 2 1 0
q×10⁴, n-caprylic acid
2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0
n-caprylic acid
Conductivity water
Absolute alcohol
0 10 20 30 40 50 60 70 80 90 100
p, cm Hg (Conductivity water and absolute alcohol)

FIGURE 12.—*Final tests in glass, capillary H*

and do not possess the same percentage accuracy as those taken at higher pressures. After data for all the other points had been taken, the pressure was dropped to zero by lowering the leveling bulb almost to the zero point and opening the lead seal at the top of the viscometer. Since the top of the liquid in the thermostat was practically on the same level as the top of the viscometer there could be no flow through the fine capillary in either direction. The apparatus was left undisturbed in this condition for 16 hours, the fine capillary being full of test liquid during the entire period. The lead cap was then screwed tight, the cross hair of the cathetometer was adjusted to be tangent to the mercury meniscus in the measuring tube, and a low pressure was suddenly applied. A stop watch was started at the same instant.

As far as the eye could judge by observing the meniscus through the microscope the liquid started flowing instantly. Since the rate of flow was so low that more than 16 minutes were required for less than 4/100,000 of a cubic centimeter of liquid to pass through the capillary, even a small abnormality in the viscosity should have been readily detected. As far as can be judged, however, the point representing this test falls accurately on the line averaging the other points. The shearing stress at the walls of the capillary was only 8.8 dynes per square centimeter for this test.

After the tests and calculations had been completed, capillaries G and H were submitted for measurement to Dr. L. V. Judson, chief of the length section of the National Bureau of Standards. His determinations of the diameters were made by the method of Shereshefsky,[24] the capillaries being sealed over at the ends and immersed in a mixture of carbon disulphide and acetone of the same refractive index as the glass. The filar screw micrometer had been checked against a calibrated stage micrometer. Two diameters of each capillary were measured, but it is not known whether these were the major or the minor axes of the ellipse or whether they were some intermediate axes. The determinations are given complete in Table 8.

TABLE 8.—*Diameters of glass capillaries (microns)* [1]

Capillary G		Capillary H	
D_1	D_2	D_1	D_2
11.00	10.94	10.82	11.14
10.98	10.80	10.68	11.02
10.97	11.01	10.88	10.91
11.03	11.09	10.65	11.08
10.96	10.97	10.91	11.00
Average 10.99	10.98	10.79	11.03

[1] The values given in this table differ slightly from the values given in the original dissertation due to a small correction which had not been applied when the original manuscript was written.

The arithmetic average of all microscopic measurements gives a value of 5.474μ for the radius, which is 0.115μ less than the average calculated radius. The maximum deviation on any single measured diameter is 0.18μ, which is essentially as great as the difference between average calculated and average measured values.

The discrepancy between the measured and calculated values for the radius of these glass capillaries is equivalent to an error of about 9 per cent in the viscosity of a liquid, but it is in the wrong direction to be accounted for on the assumption either of an adsorbed layer on the walls or of an increase in viscosity due to the fields of force of the surface molecules of the capillary. It is in the right direction to be accounted for in part by the "drainage" error which was neglected. If any theoretical significance could be attached to it other than errors of measurement, it would be that there is slip of the liquid at the walls of the capillary. There is no occasion for admitting this hypothesis, however, since the discrepancy is no greater than might

[24] J. L. Shereshefsky, A Study of Vapor Pressures in Small Capillaries, J. Am. Chem. Soc., **50**, pp. 2966-2980; 1928.

reasonably be expected from tests in and measurements of such small capillaries as here employed. There is a discrepancy of about 0.3 per cent between the values used by the National Bureau of Standards and those given by the International Critical Tables for the viscosity of such an all-important calibrating liquid as distilled water. The discrepancy of 1.4 per cent between the viscosity of benzene as found in this investigation and as quoted by the International Bureau of Physical Chemical Standards has already been referred to. Since these relatively great discrepancies exist for work done in ordinary viscometers in which it is possible to measure the diameters and the rates of flow very accurately, the error of 9 per cent is probably not excessive for the microviscometer used in this investigation. In any event the relative values for the radius of any given capillary as found by calculation for different liquids lose none of their significance from the discrepancy existing between measured and calculated radii. It can, therefore, be stated with some confidence, both for glass and platinum capillaries, that the thickness of any fixed layer adjacent to the walls is not in excess of two to three hundredths of a micron, or approximately a millionth of an inch.

V. SUMMARY AND ACKNOWLEDGMENTS

Measurements of the flow of various fatty and mineral oils through steel and nickeline capillary tubes as small as 0.18 and 0.13 mm inside radius, respectively, have shown that there is no clogging of the tubes over long periods of time when the liquids are adequately filtered. Similar measurements have been made on a much greater variety of liquids using platinum and glass capillaries as small as 9.35μ and 5.59μ inside radius, respectively. By applying to these measurements certain criteria based on the laws of simple viscous flow it has been shown that these liquids retain their ordinary bulk viscosity at least as close to the solid surfaces as two to three hundredths of a micron, or about a millionth of an inch.

In conclusion, the author wishes to express his gratitude to Profs. J. C. W. Frazer and Walter A. Patrick, of the Johns Hopkins University, and to Mayo D. Hersey and Winslow H. Herschel, of the National Bureau of Standards, for their many helpful suggestions and criticisms. He is indebted to F. G. Bitner for the sketches, and to the others whose names are mentioned in the text for the assistance they have rendered. The cost of the investigation has been defrayed in part by the Special Research Committee on Lubrication, American Society of Mechanical Engineers.

WASHINGTON, October 18, 1930.

DETERMINATION OF MAGNESIUM IN PORTLAND CEMENT AND SIMILAR MATERIALS BY THE USE OF 8-HYDROXYQUINOLINE

By J. C. Redmond and H. A. Bright

ABSTRACT

The precipitation of magnesium by the use of the reagent 8-hydroxyquinoline and titration of the acid solution of the precipitate with standard bromate-bromide solution have been studied. A procedure is given for determining magnesium in Portland cement. The method is accurate and much more rapid than the standard phosphate method.

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I. INTRODUCTION

In the method used most commonly for the determination of magnesium the latter is precipitated as magnesium ammonium phosphate. To obtain accurate results the solution containing the precipitate must be allowed to stand three to four hours, and furthermore reprecipitation [1] is necessary.

The maximum amount of magnesia (MgO) allowed by Federal specification 1a and the Standard Specification for Portland Cement (C 9–26) of The American Society for Testing Materials is 5.00 per cent (plus a tolerance of 0.4 per cent). Since a great deal of cement is purchased under these specifications, it follows that many determinations of magnesia are required. At present the phosphate method is standard, and is quite accurate and applicable for umpire analyses, but it is rather lengthy. Hence a more rapid procedure for the determination of magnesium in Portland cement is desirable, especially for routine work. The work of Berg and others indicated that 8-hydroxyquinoline might be used to advantage in a rapid method for this determination and accordingly the use of this reagent for precipitating magnesium was investigated.

Based on the results of the study a procedure has been developed for determining magnesium in Portland cements and similar materials containing not more than 5.4 per cent magnesia. In the method described, the magnesium is precipitated with 8-hydroxyquinoline and the acid solution of the precipitate is titrated with a standard solution of potassium bromate-bromide.

[1] Hillebrand and Lundell, Applied Inorganic Analysis, Wiley & Sons, pp. 512–513.

II. GENERAL CONSIDERATIONS

A number of papers have been published recently on the use of 8-hydroxyquinoline for the separation and determination of certain elements.[2] Berg states that magnesium may be precipitated in the presence of iron and aluminum in a sodium hydroxide-sodium tartrate solution. Calcium, however, accompanies the magnesium in this separation. Berg further shows that magnesium may be precipitated in the presence of calcium in a faintly ammoniacal solution, but his data indicate that reprecipitation is always necessary. These facts show that no saving of time could be made by the use of these procedures and hence it is preferable to remove the iron and aluminum with ammonium hydroxide and the calcium with ammonium oxalate as is done in the standard methods.

Rapid determinations of calcium in Portland cement can be made by direct precipitation of calcium by oxalic acid,[3] in the presence of iron and aluminum. Whether a direct precipitation of magnesium by 8-hydroxyquinoline can be made in the filtrate from such a separation of calcium was not investigated at this time. In the work discussed herein, the usual methods of separating iron and aluminum with ammonium hydroxide and calcium with ammonium oxalate were employed.

The determination of magnesium by the use of 8-hydroxyquinoline is based on the fact that magnesium and 8-hydroxyquinoline combine in dilute ammoniacal solution to form an insoluble compound, magnesium oxyquinolate, $Mg(C_9H_6ON)_2 \cdot 2H_2O$. The precipitate is crystalline and is easily filtered and washed. It may be weighed [4] as anhydrous magnesium oxyquinolate after drying at 130° to 140° C., titrated according to Koppenschaar's method for the titration of phenol,[5] or ignited under a cover of oxalic acid to magnesium oxide.[6] The work reported in this paper was confined chiefly to the titration method, since it was found that under the proper conditions the results were as accurate as those obtained by weighing, and could be arrived at much more rapidly.

Two different procedures for the precipitation of magnesium oxyquinolate are described by Berg.[7] In the first of these, the solution of the magnesium salt, containing sufficient ammonium chloride or acetate to prevent the formation of magnesium hydroxide, is made distinctly ammoniacal by adding an excess of several milliliters of concentrated ammonium hydroxide, warmed to 60° to 70° C., and the magnesium precipitated by adding a small excess of 2 per cent alcoholic or acetic acid solution of 8-hydroxyquinoline while the solution is gradually heated to the boiling point. The presence of an excess of reagent is indicated by the appearance of a yellow color in the solution. After settling, the precipitate is filtered, washed with hot dilute ammonium hydroxide (1 per cent), and either dried and weighed, or dissolved in acid and titrated. This procedure is here-

[2] Berg., Z. Anal. Chem., **70**, p. 34; 1927; **71**, pp. 23, 369; 1927. Berg. Pharm. Zeit., 1929. Hahn and Vieweg. Z. Anal. Chem., **71**, p. 122; 1927. J. Robitschek, J. Am. Cer. Soc., **11**, p. 587; 1928. Lundell and Knowles, B. S. Jour. Research, **3**, p. 91; 1929.
[3] R. K. Meade, Portland Cement, p. 189; 1906.
[4] In which case the precipitate should be filtered on a Jena glass or Gooch crucible.
[5] Koppenschaar, Z. Anal. Chem., **15**, p. 223; 1876.
[6] Hillebrand and Lundell, Applied Inorganic Analysis, Wiley & Sons, p. 115.
[7] Z. Anal. Chem., **71**, p. 27; 1927.

after referred to as procedure 1. In the second procedure [8] an excess of 8-hydroxyquinoline solution is added to the acid solution containing the magnesium and sufficient ammonium salts to prevent the precipitation of magnesium hydroxide. The solution is then heated to boiling, and an excess (2 to 3 ml) of concentrated ammonium hydroxide is added. The supernatant liquid should be yellow. If not, more 8-hydroxyquinoline is added until the yellow color is obtained. After settling, the precipitate is filtered, and treated as in procedure 1. This procedure is designated hereinafter as procedure 2.

It will be noted that the essential difference between the two methods of precipitation is that in procedure 1 the magnesium is precipitated by adding the reagent to an ammoniacal solution while in procedure 2 ammonium hydroxide is added to an acid solution to which the reagent has previously been added.

III. EXPERIMENTAL STUDY

For studying the conditions affecting the precipitation of magnesium by 8-hydroxyquinoline various amounts of a standard solution of magnesium chloride were used. This standard solution was prepared from magnesium chloride of good reagent quality and was standardized by precipitating the magnesium as magnesium ammonium phosphate, reprecipitating, and igniting to the pyrophosphate. The titration procedure and the solutions of 8-hydroxyquinoline, potassium-bromide, etc., were those described later under the method for Portland cement.

The results of preliminary tests showed that boiling the solutions was not entirely satisfactory in that the magnesium oxyquinolate tends to creep, and the reagent tends to volatilize, but that the elimination of the heating to boiling produced low results. Stirring was found to accelerate precipitation. It was noted that if a large excess of reagent was added results were high. It was further noted that the time required for complete precipitation was influenced by the conditions under which the 8-hydroxyquinoline was added.

A series of experiments was accordingly made in which the acid solution, containing an excess of 8-hydroxyquinoline, was made ammoniacal. All test solutions also contained ammonium salts and a small amount of ammonium oxalate to simulate the conditions under which the magnesium precipitation is usually carried out in the analysis of Portland cement. Some of the tests were made exactly as described in procedure 2, while others, precipitated similarly, were digested for longer periods of time. All precipitations in this series and the following ones were made in a volume of about 350 ml, which is approximately that of the filtrate from the calcium determination in the analysis of Portland cement. The results are given in Table 1.

[8] Pharm. Zeit.; 1929.

TABLE 1.—*Results for MgO obtained by adding an excess of NH_4OH to an acid solution containing 8-hydroxyquinoline*

[Procedure 2]

Experiment No.	MgO taken	MgO found	Error	Reagent added	Approximate reagent required	Approximate excess	Remarks
	g	*g*	*g*	*ml*	*ml*	*ml*	
1	0.0048	0.0036	−0.0012	20	3	17	Filtered 15 minutes after addition of reagent.
2	.0120	.0081	−.0039	20	7	13	
3	.0288	.0241	−.0037	20	17	3	
4	.0048	.0037	−.0011	20	3	17	Solution digested for 1 hour on steam bath.
5	.0120	.0112	−.0008	20	7	13	
6	.0288	.0273	−.0015	20	17	3	
7	.0048	.0047	−.0001	20	3	17	Solution digested for 2 hours on steam bath and then allowed to stand at room temperature over night.
8	.0120	.0119	−.0001	20	7	13	
9	.0288	.0287	−.0001	20	17	3	

In a second series of tests the 8-hydroxyquinoline reagent was added to the warm ammoniacal solution; that is, according to procedure 1. The results are shown in Table 2.

TABLE 2.—*Results for MgO obtained by adding an excess of 8-hydroxyquinoline to an ammoniacal solution*

[Procedure 1]

Experiment No.	MgO taken	MgO found	Error	Reagent added	Approximate reagent required	Approximate excess
	g	*g*	*g*	*ml*	*ml*	*ml*
10	0.0048	0.0043	−0.0005	20	3	17
11	.0049	.0048	−.0001	28	3	25
12	.0120	.0115	−.0005	20	7	13
13	.0121	.0115	−.0006	22	7	15
14	.0121	.0120	−.0001	32	7	25
15	.0121	.0123	+.0002	40	7	33
16	.0170	.0166	−.0004	31	10	21
17	.0288	.0272	−.0016	20	17	3
18	.0291	.0294	+.0003	31	17	14
19	.0291	.0293	+.0002	40	17	23
20	.0291	[1] .0297	+.0006	20	17	3

[1] Stirring substituted for boiling.

As previously mentioned, complete precipitation was obtained in much less time when the solutions were stirred. Furthermore, a much smaller excess of reagent was requred for complete precipitation in a short time. It was observed, however, that high values were obtained when the hot ammoniacal solution was stirred and the 8-hydroxyquinoline added until a precipitate first appeared. Under these conditions which correspond essentially to those of procedure 1, with the exception that stirring is substituted for "the heating to boiling," a considerable excess of reagent must be added before the precipitate begins to form. The results obtained when the heating to boiling was replaced by stirring in procedure 2 were satisfactory, since only small positive errors were noted with the same excess of reagent that caused large errors in the previously mentioned case.

This latter method will be designated as procedure 3, and is carried out as follows: All of the reagent is added to a warm (60° to 70° C.) neutral or faintly ammoniacal solution, and an excess of ammonium hydroxide of 3 to 4 ml per 100 ml of the solution is added. The solution is then stirred for 10 minutes. The results obtained by this method of precipitation, procedure 3, are given in Table 3.

TABLE 3.—*Results for MgO obtained by adding an excess of 8-hydroxyquinoline reagent to the neutral (or slightly ammoniacal) solution at 60° to 70° C., then a 3 to 4 per cent excess of NH_4OH, then stirring for 10 to 15 minutes*

[Procedure 3]

Experiment No.	MgO taken	MgO found	Error	Reagent added	Approximate reagent required	Approximate excess
	g	*g*	*g*	*ml*	*ml*	*ml*
21	0.0048	0.0052	+0.0004	20	3	17
22	.0120	.0123	+.0003	20	7	13
23	.0120	.0129	+.0009	35	7	28
24	.0123	[1].0124	+.0001	32	7	25
25	.0170	.0172	+.0002	20	10	10
26	.0240	.0260	+.0020	40	14	26
27	.0224	[1].0223	+.0001	40	14	26
28	.0288	.0288	.0000	20	17	3

[1] Precipitate dried 1 hour at 130° to 140° C. before titration.

Passing on to a further consideration of the data given in Tables 1, 2, and 3, the following will be observed: In Table 1 experiments 1 to 3 show that with 20 ml of the 8-hydroxyquinoline solution (1.25 per cent) complete precipitation of magnesium was not secured in 15 minutes when the acid solution of magnesium and 8-hydroxyquinoline is treated with ammonium hydroxide (procedure 2). With additional digestion and long standing, precipitation is complete. Twenty milliliters of the reagent 8-hydroxyquinoline is theoretically more than sufficient to precipitate from a 0.5 sample, the maximum amount of magnesia (5.4 per cent) allowed by either the Federal specification No. 1a for Portland Cement, or The American Society for Testing Materials Specification for Portland Cement (C 9–26).[9]

In Table 2, experiments 10, 12, and 17 also show that 20 ml of 8-hydroxyquinoline reagent is not sufficient to secure complete precipitation of magnesium when the 8-hydroxyquinoline reagent is added to the ammoniacal solution (procedure 1), though precipitation is more nearly complete than in the case when ammonium hydroxide was added to the acid solution of magnesium containing the 8-hydroxyquinoline reagent. Increasing the excess of reagent aids in securing complete precipitation within a short time. With an excess of approximately 25 ml of 8-hydroxyquinoline reagent small amounts of magnesium are completely precipitated by procedure 1 (experiments 11, 14, and 19). Furthermore, this excess of reagent does not introduce any serious positive error when 0.0291 g of magnesia are present as shown by experiment 19. With a cement of unknown magnesium content, it is therefore possible, when using this procedure to add from 35 to 40 ml of the reagent, thereby insuring complete precipitation for cements low in magnesia and at the same time intro-

[9] A. S. T. M. Standards II, p. 27; 1927.

ducing no serious positive error for those cements approaching the maximum amount (0.0270 g for a 0.5 sample) of magnesia allowed by the standard specifications. A comparison of the results of experiments 17 and 20 shows the effect of stirring in hastening complete precipitation. A further comparison of experiment 20 with 28 shows the positive error introduced by the stirring procedure when the 8-hydroxyquinoline reagent is added to a hot ammoniacal solution.

In Table 3, it will be noted (experiment 28) that 20 ml of the 8-hydroxyquinoline reagent is sufficient to precipitate 0.0288 g of magnesia when added to a neutral or faintly ammoniacal solution, followed by the addition of an excess of 3 to 4 per cent of ammonium hydroxide and stirring of the solution for 10 to 15 minutes (procedure 3). Excess reagent apparently tends toward larger positive errors in this procedure (procedure 3). As indicated in experiments 21, 22 and 25, the error, when 20 ml of reagent is added, is negligible for commercial analyses. These positive errors are probably due to occluded reagent and can be avoided if the precipitate is dried at 130° to 140° C. before it is weighed or titrated since 8-hydroxyquinoline is volatile at these temperatures. Experiments 24 and 27 support this view.

From the preceding discussion it is evident that less reagent is required for complete precipitation in a short time if the solution is stirred. Furthermore, in cases where the approximate magnesia content of a cement is not known, it is satisfactory to add 20 ml of the reagent, since this amount gives satisfactory results for quantities of magnesia from 0.0048 to 0.0288 g. This procedure has accordingly been adopted in the method to be described. In this method silica need not be removed and only single precipitations of iron and aluminum, and of calcium are made. The very small amount of magnesia which may be occluded in the R_2O_3 and calcium precipitates is apparently compensated for by the tendency of the method to give results which are a few tenths of a milligram high.

TABLE 4.—*Results obtained by recommended procedure on standard argillaceous limestone No. 1a*

Experiment No.	Weight of sample	MgO present	MgO found	Error
	g	g	g	g
29	0.5	0.0109	0.0108	−0.0001
30	.5	.0109	.0109	.0000
31	.8	.0175	.0174	−.0001
32	.8	.0175	.0176	+.0001
33	.8	.0175	.0176	+.0001
34	.8	.0175	.0177	+.0002

The performance of the method is illustrated by the data given in Table 4. Since the bureau issues no standard analyzed sample of Portland cement because of the inconstancy of the chemical composition of this material, and since the preparation of such a standard for this work would have involved a large number of determinations, samples of Bureau of Standards standard argillaceous limestone No. 1a were used to test the results obtained with the method. This limestone, when ignited in a platinum crucible for 30 minutes at 1,100° C., has a composition very similar to Portland cement. After this

ignition, the samples were dissolved in hydrochloric acid, and the magnesia was then determined by the recommended method. By using the method described below an experienced operator can determine magnesia in a Portland cement or limestone in 1.5 to 2 hours.

IV. THE METHOD FOR PORTLAND CEMENT

1. SOLUTIONS REQUIRED

Acetic acid solution of 8-hydroxyquinoline (1.25 per cent).—Dissolve 25 g of 8-hydroxyquinoline in 60 ml of glacial acetic acid. When solution is complete dilute to a volume of 2 liters with cold water. One milliliter of this solution is equivalent to 0.0016 g of MgO.

Potassium bromate-bromide solution (0.2 N).—Dissolve 20.00 g of potassium bromide and 5.57 g of potassium bromate in 200 ml of water and dilute to 1 liter. The ratio of this solution to the standard sodium thiosulphate solution is obtained as follows: To 200 ml of water in a 400-ml beaker add 20 ml of hydrochloric acid (specific gravity 1.19) and then exactly 25 ml of the potassium bromate-bromide solution. Add immediately 10 ml of the potassium iodide solution and titrate with the standard sodium thiosulphate solution until the solution is nearly colorless. Then add 2 ml of starch solution and titrate to the disappearance of the blue color.

Sodium thiosulphate solution (0.1 N).—Dissolve 25 g of sodium thiosulphate ($Na_2S_2O_3.5H_2O$) in 200 ml of water, and dilute to 1 liter. Standardize this solution with a 0.1 *N* solution of resublimed iodine. The iodine solution is standardized with Bureau of Standards standard sample of arsenious oxide No. 83. One milliliter of an exactly 0.1 *N* sodium thiosulphate solution is equivalent to 0.000504 g of MgO.

Potassium iodide solution (25 per cent).—Dissolve 25 g of potassium iodide in 100 ml of water.

Starch solution.—Dissolve 5 g of soluble starch and 2.5 g of salicylic acid in 1 liter of water.

2. PROCEDURE

To a 0.500 g sample in a 400 ml beaker add 10 ml of water and 10 ml of hydrochloric acid (specific gravity 1.19). Heat gently, and grind any coarse particles with the flattened end of a glass rod until decomposition is complete. Dilute to 150 ml with hot water.

To the solution add three drops of methyl red indicator (0.2 per cent alcoholic solution), and then ammonium hydroxide (specific gravity 0.90) until the solution is distinctly yellow. Add macerated filter paper and heat to boiling. Boil for one to two minutes, remove from the hot plate, and allow the solution to stand until the precipitate has settled. Filter without delay and wash the precipitate thoroughly with a hot 2 per cent solution of ammonium chloride. To the filtrate add 1 ml of ammonium hydroxide (specific gravity 0.90), and heat to boiling. When the solution is boiling, add 25 ml of hot ammonium oxalate solution (4 per cent), and continue the boiling for two or three minutes. Digest on the steam bath for one-half to one hour and then filter and wash five or six times with warm water. The volume of the filtrate at this point should be about 350 ml.

Heat the filtrate to 60° to 70° C. and add [10] 20 ml of the 8-hydroxyquinoline solution, and then 4 ml of ammonium hydroxide per 100 ml of solution. Stir on a mechanical stirring machine for 10 to 15 minutes and set aside until the precipitate has settled. Filter and wash with hot dilute ammonium hydroxide (1:40). Dissolve the precipitate in 50 to 75 ml of hot dilute hydrochloric acid (1:9), dilute the resulting solution to 200 ml, and add 15 ml of hydrochloric acid (specific gravity 1.19). Cool to 25° C. and add from a pipette 25 ml of the standard potassium bromate-bromide solution. Add immediately 10 ml of potassium iodide solution and titrate with the sodium thiosulphate solution until the solution clears slightly.[11] Add 2 ml of the starch solution and titrate to the disappearance of the blue color.

The percentage of magnesia may be calculated as follows:

If

A = g of MgO per ml of the standard thiosulphate solution.

B = ml of thiosulphate solution equivalent to 25 ml of the bromate-bromide solution.

C = ml of thiosulphate solution required for titrating the precipitate.

Then

$$(B-C)\times A = \text{g of MgO}$$

For example

If 25 ml of the bromate solution required 49.85 ml of 0.1008 N thiosulphate solution and 13.45 ml of the thiosulphate solution were required for titrating the precipitate, the percentage of magnesia in a 0.5 g sample would be calculated thus:

$$(49.85-13.45)\times 0.000508 = 0.0185 \text{ g MgO}$$

$$0.0185\times\frac{100}{0.5} = 3.70 \text{ per cent MgO}$$

V. ACKNOWLEDGMENT

Acknowledgment is made to R. B. Rudy, who cooperated with the senior author in preliminary tests on the use of the reagent 8-hydroxyquinoline in determining magnesia in Portland cement. Because of Mr. Rudy's assignment to other work the study of the reaction and the development of the recommended procedure were made by the senior author with the assistance of the junior author.

WASHINGTON, August 15, 1930.

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[10] If a mechanical stirrer is not available the following procedure may be substituted at this point: Heat the filtrate to 60° to 70° C. and add 4 ml of ammonium hydroxide (specific gravity 0.90) per 100 ml of solution. Then add 40 ml of 8-hydroxyquinoline solution and heat to boiling. As soon as the solution boils, set it aside until the precipitate settles, filter, and treat as in the recommended procedure.

[11] The reactions involved in the titration are as follows: Hydrochloric acid reacts with the potassium bromate-bromide solution liberating free bromine according to the equation—

$$KBrO_3+5KBr+6HCl=6KCl+3H_2O+3Br_2$$

The free bromine reacts with the 8-hydroxyquinoline in solution forming dibromohydroxyquinolate, as follows—

$$C_9H_7OH+2Br_2=C_9H_5OHBr_2+2HBr$$

On addition of the potassium iodide solution the excess of free bromine is replaced by free iodine which is titrated with a standard solution of sodium thiosulphate.

AN IMPROVED APPARATUS AND METHOD FOR THE ANALYSIS OF GAS MIXTURES BY COMBUSTION AND ABSORPTION

By Martin Shepherd

ABSTRACT

This paper describes an improved volumetric apparatus for the analysis of gases by combustion and absorption methods. The apparatus is of the type which has a series of pipettes connected to the burette and is commonly called an "Orsat." The operating technique is given in a set of simple instructions.

While the unit is similar to many commercial forms of gas analysis apparatus, it differs in a number of details of the assembly and the construction of individual parts. The adjustment and control of pressure balances have been greatly improved. Distinct advances have been made in the designs of the combustion and absorption pipettes, and of the manometer-compensator unit. A new type of mounting permits the easy removal and replacement of any part.

The unit as a whole has been made as modern as possible. It has been found more satisfactory, both as to accuracy obtainable and ease of manipulation, than other available models.

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I. INTRODUCTION

The gas analysis unit described in this paper represents a development which occurred over a number of years, during which time the apparatus was in the hands of several investigators. It is consequently impossible to assign full credit for the present design to any one

individual. The author desires to express his indebtedness to E. R. Weaver and P. G. Ledig, to whose work special reference is made later in the paper. He is also much indebted to E. O. Sperling, glass blower of this bureau, for many helpful suggestions. Some of the better features common to many types of so-called "Orsat" apparatus have been retained.

II. THE IMPORTANCE OF APPARATUS DESIGN IN GAS ANALYSIS

Gas analysis differs from other chemical analysis in the relative importance of the apparatus as compared to the procedure used in the analysis. A gas analysis unit must necessarily be comparatively extensive and complicated in order to perform a simple analysis. The effort devoted to apparatus design is an important and often a major part of the work. The present generally unsatisfactory state of gas analysis is attributable, in a considerable measure, to poorly designed apparatus. A number of very common errors of gas analysis are inherent in the apparatus rather than in the method used. In addition, awkward details of manipulation are too frequently encountered. The unit to be described was designed largely to correct these common faults.

III. DESCRIPTION OF THE APPARATUS

In describing this apparatus, each part will be discussed separately, and its advantages noted. The general assembly will then be explained. Reference will be made to drawings, which are presented with sufficient detail to permit reproduction of the apparatus in any laboratory or shop. For convenience, the assembly drawing has been lettered to correspond to the lettering of the drawings of the individual parts.

1. THE BURETTE

The common fault of burettes supplied with many gas analysis apparatus lies in the fact that the graduations are extended less than one-half way around the circumference. Because this system of graduation does not permit the elimination of parallax, serious errors are introduced in reading the volumes. The burette illustrated in Figure 1 is graduated according to the National Bureau of Standards specifications for volumetric burettes.[1] All marks are extended slightly over half way around the circumference. Graduations corresponding to odd numbered milliliters are extended three-fourths way around, and those corresponding to even numbered milliliters are extended completely around. This system of graduation produces a burette which may be read conveniently and without parallax. The length of the graduated section of the burette is approximately 60 cm, so that the distance between marks is about 1.2 mm, which accords with the bureau's specifications. A burette of this size is conveniently read, and the attached stopcocks are easily accessible. If a much longer burette is used, no real gain in accuracy is obtained, and some inconvenience in reading and manipulation may be experienced.

[1] B. S. Circular No. 9, p. 5.

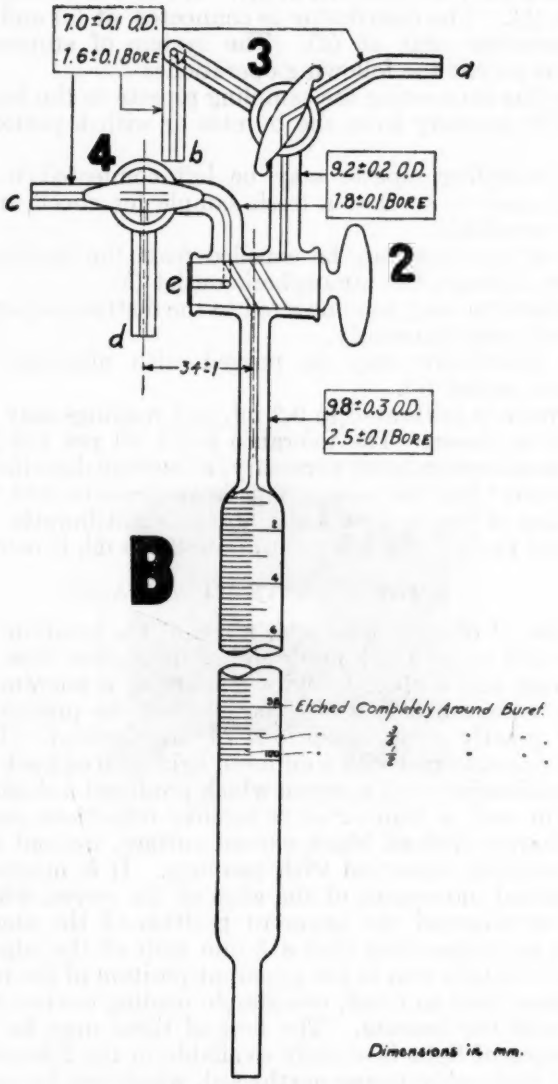

FIGURE 1.—*The burette*

Length of graduated section, 620±20 mm.
Length of capillary from graduated section to bottom of stopcock *2*, 50±5 mm.
Length of section from 100 ml mark to tapered outlet, 50±10 mm.
Length of barrel of stopcock *2*, 40 to 43 mm.
Diameter of key of stopcock *2*, at center, 13.5 to 14.0 mm.
Length of barrels of stopcocks *3* and *4*, 35 to 37 mm.
Diameter of keys of stopcocks *3* and *4*, at center, 12.5 to 13 mm.
Outlets c and *d* to be ground flat and slightly bevelled at the outer rim.

The burette is shown in Figure 1. The pipette containing the sample to be analyzed is connected at (*a*). A small beaker is placed under the outlet (*b*). The distributor is connected at (*c*) and the manometer-compensator unit at (*d*). The system of stopcocks *2–3–4* is designed to permit the following operations:

1. The line connecting the sampling pipette to the burette may be flushed with mercury from the burette or with a portion of the gas sample.
2. The sampling pipette may be left connected to the burette during an analysis so that a fresh sample for check analysis is immediately available.
3. Gas or mercury may be expelled from the burette, and water introduced, through the atmospheric outlet (*b*).
4. The burette may be connected to the distributor, or the manometer, or both simultaneously.
5. The distributor may be purged with nitrogen through the atmospheric outlet (*e*).

The burette is calibrated to 0.2 ml, and readings may be estimated to 0.05 ml or closer. The tolerance is 0.1 ml per 100 ml. If more accurate measurements are necessary, a burette described by Weaver and Shepherd [2] may be used. This is accurate to 0.01 ml. For the investigation of gas analysis methods, a weight burette developed by Weaver and Ledig,[3] which is accurate to 0.003 ml, is recommended.

2. THE BURETTE ILLUMINATOR

A number of observations were made of the position of a mercury meniscus with respect to a mark etched on a glass tube, using both a cathetometer and a special device employing a micrometer screw to move the meniscus. It was apparent that the precision attainable depended greatly upon conditions of illumination. The optimum condition was obtained with a diffiused light, placed back of the meniscus, in combination with a screen which produced a shadow across the meniscus in such a manner as to remove reflections and produce in effect a sharply defined black curved surface, instead of the mirror surface ordinarily observed with mercury. It is interesting to note that a vertical movement of the edge of the screen which produced this shadow changed the apparent position of the meniscus. This effect was so pronounced that a 5 mm shift of the edge produced a shift of 0.01 to 0.02 mm in the apparent position of the meniscus.

With these facts in mind, two simple reading devices were made to be used with the burette. The first of these may be used when a proper source of light is already available in the laboratory, such as a window, preferably facing northward, which can be covered with a sheet of ordinary tracing cloth. This provides excellent illumination. The simple shield shown in Figure 2 provides the shadow. It is made of sheet metal bent to fit the water jacket surrounding the burette, and is lined with black felt and finished with "optical black" lacquer. The upper edge of the slot is adjusted by hand to a position approximately one graduation above the meniscus of the mercury within the burette. Under these conditions the observer will be able to make readings of the position of the meniscus with satisfactory precision.

[2] E. R. Weaver and Martin Shepherd, A Burette for the Accurate Measurement of Gas Volumes without Gas Connection to a Compensator. B. S. Sci. Paper No. 559.

[3] E. R. Weaver and P. G. Ledig, A Weight Burette for Gas Analysis, J. Am. Chem. Soc., **42**, p. 1177; 1920.

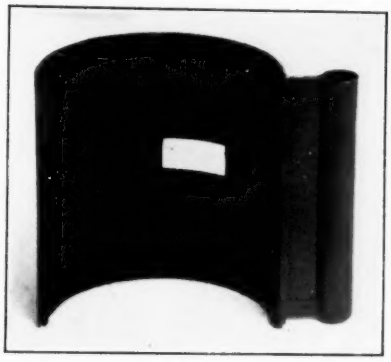

FIGURE 2.—*The burette reading shield*

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FIGURE 3.—*The burette illuminator (front and side views)*

When the laboratory is not supplied with a suitable source of diffused light, or when the apparatus is to be carried from place to place or used at night, a lamp mounted upon the frame supporting the apparatus is very convenient. An arrangement which provides excellent illumination is shown in Figure 3. The lamp (*l*) is mounted permanently at the top of the apparatus, and its light concentrated by a condenser lens (*g*). The beam falls upon a sliding mirror (*m*) placed at 45° to the source and the burette. The front surface of the mirror is finely ground, and a slotted shield (*h*) is placed before the mirror in order to throw a shadow upon the meniscus as before. A sheet metal shield (*f*) shades the lamp. The mirror and shield slide freely upon the rod (*j*), the split clamp (*i*) being adjusted to sufficient tension to just support their weight. The burette illuminator is fastened to the apparatus frame at (*f*) and (*k*).

3. THE MANOMETER AND COMPENSATOR

The manometer and compensator are constructed as one unit. This construction presents a number of advantages. The unit is compact and may be removed from the water jacket without disturbing the burette or distributor. It is much less fragile than the usual type. Connection from the compensator to the atmosphere is made without the ordinary stopcock. Other advantages will become apparent after a study of the detailed drawing of the upper part of the manometer-compensator unit, shown in Figure 4.

The balance point of the manometer is obtained by electric contact. This method was suggested by Gregg [4] and its accuracy determined by Weaver and Ledig,[5] but it has not received the attention it merits. For the purpose used here it is by far the most satisfactory means of adjusting the pressure to a zero or fixed reference point with respect to both accuracy and ease of manipulation. A platinum lead (*o*) is sealed into the arm of the manometer adjacent to the compensator and passes through a small tube (*q*) in the dome of the compensator. A platinum contact (*n*), sharpened and polished to a needle point, is supported by the sleeve *A* so that it centers within the same arm of the manometer, as shown in the drawing. Mercury is used as the manometer fluid. When the mercury meniscus rises to touch the point of the contact (*n*) an electric circuit,

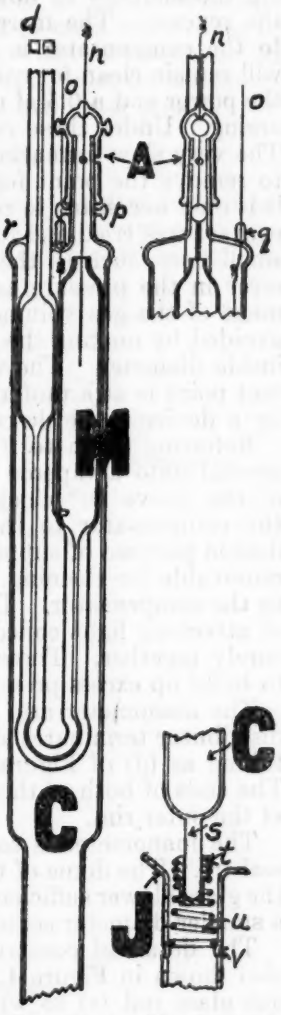

FIGURE 4.—*The manometer-compensator unit*

Inside diameter of manometer arms, 9±1 mm.
Inside diameter of capillary U connecting manometer arms, 1.5 to 2 mm.
Total length of manometer from r to bottom of capillary U, 100±10 m'm.
Length of compensator arm of manometer (left arm) 50±5 mm. Diameter of compensator below manometer=diameter of the burette.

[4] J. Ind. Eng. Chem., **9**, p. 528; 1917.

[5] J. Am. Chem. Soc., **42**, p. 1177; 1920.

including a miniature lamp, is closed. The flash of the lamp indicates the balance point. The balance is always obtained by allowing the mercury to flow upward toward the platinum point—never the reverse. The mercury in this arm of the manometer adjacent to the compensator is not in contact with stopcock lubricant and will remain clean for considerable periods. A 3-volt battery supplies the power and a 0.5 μf condenser is placed across the leads to prevent arcing. Under these conditions the platinum contact will not foul. The very slow formation of a platinum amalgam makes it necessary to remove the point for cleaning once or twice a year. To do this it is only necessary to remove the supporting sleeve *A*. (A tungsten contact was tried and found altogether unreliable.) A manometer of small bore, such as the type in common use, will cause appreciable error in the pressure adjustment and consequently in the measurement of the gas volumes. Any significant capillary error has been avoided by making the manometer arms from tubing of 9 to 10 mm. inside diameter. The upward flow of the mercury toward the contact point is at a uniform and very slow rate. This is accomplished by a device to be described in the following section.

Referring again to Figure 4, it will be seen that the sleeve *A* is ground onto a tapered outlet of the compensator dome. Rotation of the sleeve 90° clockwise from the position shown will connect the compensator to the atmosphere. The sleeve then serves the double purpose of supporting the platinum point, making this easily removable for cleaning, and replacing the stopcock usually attached to the compensator. The glass buttons or hooks (*p*) provide means of attaching light coiled springs which hold the ground surfaces securely together. These will not be necessary if care is taken never to build up excess pressure within the compensator.

The manometer arm which is to be connected to the burette and distributor terminates at (*d*) in a capillary cut from the same piece of tubing as (*d*) of Figure 1, to which it is joined by a rubber sleeve. The ends of both of these tubes are ground flat and slightly bevelled at the outer rim.

The manometer is sealed into the compensator through the ring seal (r). The dome of the compensator is slightly enlarged to permit the glass blower sufficient latitude. The compensator is drawn off to a smaller diameter somewhat below the lower end of the manometer.

The detail of construction of the bottom of the compensator is also shown in Figure 4. The compensator terminates in the drawn out glass rod (*s*) to which is cemented the metal sleeve (*t*). This sleeve is threaded on the outside, and the spring (*u*) is screwed into this threaded part. These metal parts are chromium plated. *J* represents a portion of the lower end of the water jacket, which terminates here in a constricted tube (*v*). The spring fits snugly within this tube and rests upon the constriction. This supports a part of the weight of the compensator and prevents it from swaying within the water jacket. The remainder of the weight of the combined manometer and compensator is supported by the buoyant force exerted by the water within the jacket.

The manometer and compensator may be blown separately. This arrangement was used by Mr. Ledig and is shown in Figure 5. The platinum contact point (*n*) is cemented into the manometer as shown.

This could be improved by substituting a ground sleeve at this point and eliminating the stopcock. This construction is more easily achieved in the hands of the amateur glass blower, and is illustrated for this reason. It is more fragile than the combined unit, and ordinarily can not be removed from the water jacket without disconnecting other parts of the apparatus. However, it is a distinct improvement over the manometer usually placed outside of the water jacket.

4. THE PRESSURE CONTROL

In order to transfer gas from one part of the apparatus to another and to balance the manometer, some method of pressure control is necessary. This usually consists of a vertical movement of the

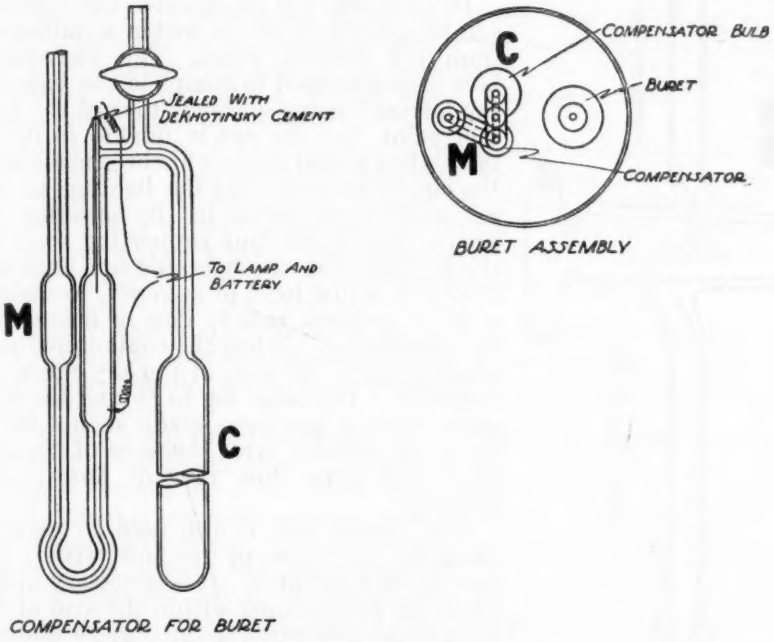

FIGURE 5.—*Manometer and compensator as separate units (Ledig)*

The assembly within the water jacket is also shown.

leveling bulb which supplies the confining fluid to the burette, and this adjustment is ordinarily made by raising and lowering this reservoir by hand or by some gear system. The latter is cumbersome, and the former both awkward and inaccurate.

Many years' use of the following method has shown it to be simple and accurate. Four rings are fixed to the frame supporting the apparatus. When the leveling bulb is placed on the uppermost of these rings and the burette opened to the atmosphere, mercury from the bulb will completely fill the burette. When the bulb is placed on the lowest ring and the burette opened to the atmosphere, the mercury within the burette will fall to a level a little below the 100 ml mark.

The remaining two rings are fixed at equal distances between the first two. Mercury may then be introduced or withdrawn from the burette by placing the leveling bulb on the proper ring. The pressure control is obtained by regulating the rate of flow of mercury into and out of the burette. This is accomplished by interposing a special control stopcock [6] between the burette and the mercury reservoir. The stopcock is illustrated in Figure 6. The key of this cock has two bores, one of which is provided with the fine constriction shown. Rough adjustments are made through the large bore, following which a 90° turn of the key admits an extremely slow flow of mercury to the burette.

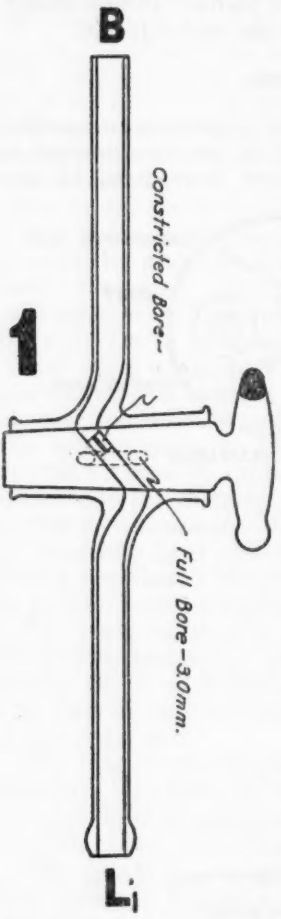

FIGURE 6.—*The control stopcock*

The stopcock connects to the burette at *B* and to the levelling bulb at L_1. Length of barrel, 40 to 43 mm. Diameter of key at center, 14 mm. The constriction is 2 to 3 mm in length and will pass a wire 0.125 mm in diameter, but will not pass a wire 0.15 mm in diameter.

In balancing the manometer the mercury can be quickly raised to within a millimeter from the contact point. The constricted bore is then opened to complete the balance, the mercury rising so slowly toward the contact point that the eye is unable to determine when actual contact has been made until the circuit is closed and the lighting of the miniature lamp reveals it. By selecting the proper one of the four supporting rings for the leveling bulb the operator can maintain a roughly equal head of mercury, so causing a fairly uniform rate of flow of mercury in the manometer. When the contact has been made another 90° turn of the key closes the stopcock. The time lag in closing the cock after contact has been made should result in no significant error, because of the uniform and very slow rate of flow of the mercury.

The control cock is also used to regulate pressures and rates of gas flow within the rest of the apparatus. It is necessary to displace the gas confined within the arm of the manometer connected to the burette and the distributor before passage to any of the pipettes, thus eliminating the errors which will otherwise arise from diffusion of gases into the manometer. The thread of mercury in the capillary exit of the manometer may be safely raised to the bore of the connecting stopcock (*4* of fig. 1) by using the constricted bore of the control cock. There is thus no danger of emptying the mercury from the manometer into the distributor. The same control is used in displacing gas from the pipettes. It is possible to bring the reagents within the pipettes to etched marks on the capillary exits without danger of drawing reagent into the distributor. For difficult combustions, such as those

[6] Described in detail in a note, A Simple Control Stopcock for Gas Analysis Apparatus, by Martin Shepherd, B. S. Jour. Research 4, p. 23 (RP130); 1930.

involving acetylene, ethylene, ethane, propane, and heavy hydrocarbons, where thermal decomposition with the deposition of carbon is apt to occur, a very slow rate of flow of the combustible gas into the combustion pipette is necessary, and is readily insured by use of the control cock.

The stopcock can be made in several ways. The glass blower may seal a No. 37 (B. & S. gage) copper wire into the solid key and along the axis of one bore. The key is then drilled out from opposite sides, leaving an undrilled segment 2 to 3 mm in thickness just off the center of the key. Nitric acid is used to remove the copper wire from the undrilled portion. A second method is as follows: Draw down a 6 to 7 mm glass tube so that one end is sealed shut and the outside diameter of the tube fits snugly into the ordinary 3 mm bore of the stopcock key. Cut or grind off the end of this tube, beginning at the point where the tube first opens into a fine capillary, and continue until the capillary will permit the passage of a No. 38 (B. & S. gage) wire, but will not pass a No. 36 wire. (The gage wire is inserted from the large end of the tube.) The constriction is now of the proper size, and a section of 2 to 3 mm in length should be cut from the tube at this point. This section is cemented within the ordinary bore of the stopcock. DeKhotinsky cement is suitable, and should be applied to the outside of the section, which is then slipped into the bore of the stopcock key. The key is then placed in an electric oven, heated slowly to 130° C., and then allowed to slowly cool to room temperature within the oven.

The fine constriction must be set within the bore of the key and away from the outside surface as shown in the drawing. When this is done no trouble results from plugging of the constriction by the stopcock lubricant.

It is important that the position of the key of all control stopcocks should be made uniform. Experience has shown that the most desirable orientation is as follows: One end of the handle of the key should be marked with colored glass, a bright paint or a knob as shown on the drawing. If the stopcock is attached to the burette in the position shown, the indicating end of the handle should point upward when the key is turned to open the constriction. It should point outward (toward the reader) when the key is turned to open the full bore, and inward (away from the reader) when the key is turned to close the stopcock. If these directions are observed, the operator will soon accustom himself to these positions, and will not be at a loss when operating another apparatus with similar control.

5. THE WATER JACKET

The water jacket of the usual gas analysis apparatus has a large rubber stopper at the lower end. The burette projects through a hole in this stopper, and the lower end of the compensator may or may not be supported by a cup in the stopper. This stopper has seemed to be an inconvenient necessity. The stopper may leak, drop out of place, split the jacket if thrust in too tightly, or stick to the jacket so that its removal therefrom is a questionable operation. Two means of eliminating the troublesome stopper are offered. Both are illustrated in Figure 7.

The first of these consists of a molded rubber sleeve (x), made from sulphur-free rubber. This fits over the outlet (w) of the water jacket. The burette B slips loosely through the outlet and is then gripped by the smaller bore of the rubber sleeve. The control stopcock (1) is also secured in place within the smaller bore of the sleeve, so that its end butts against the lower end of the burette. This eliminates all of the undesirable features of the large stopper with the exception of the tendency of the rubber to stick to the glass. If this occurs it

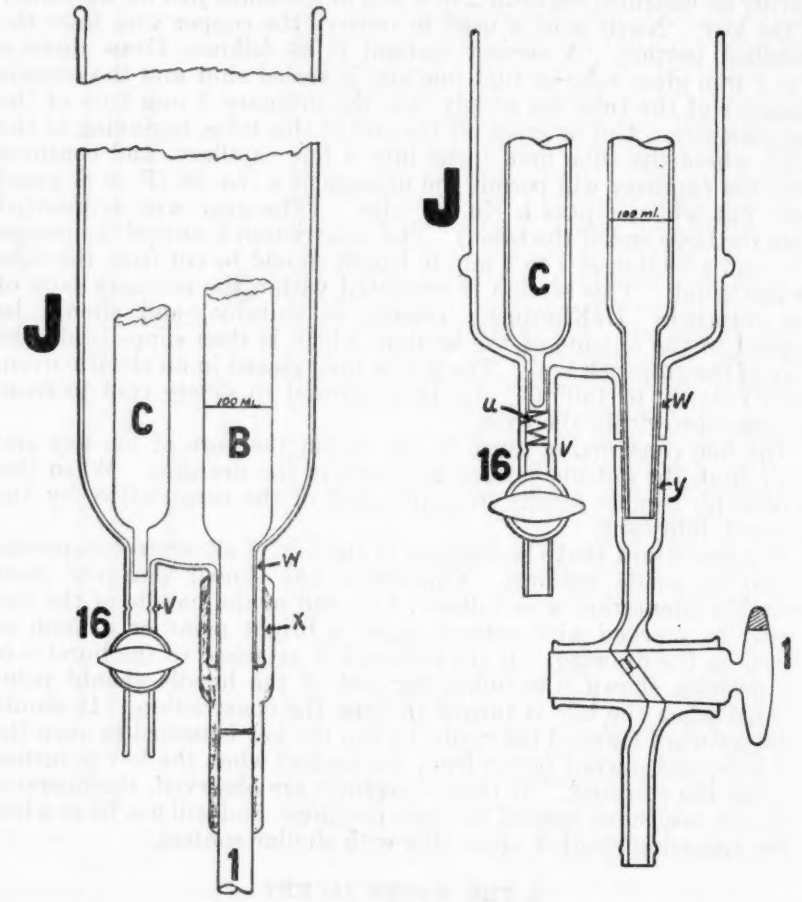

FIGURE 7.—*The water jacket*

Two methods of assembling the burette and control stopcock are shown. Diameter of jacket, 70 to 75 mm.

will, of course, be necessary to cut the sleeve to remove it and subsequently replace it with a new one.

The second method involves a slightly more difficult construction, but eliminates the two objections of the possibility of the rubber sleeve sticking to the glass and the necessity of eventually replacing it. The outlet of the water jacket (w) is tapered but not ground. The lower end of the burette is tapered to fit loosely inside of the outlet.

The upper lead from the control stopcock is flared (*y*) to loosely fit the lower portion of the tapered burette. These parts are cemented together by warming gently and applying DeKhotinsky cement until it flows smoothly around the spaces between (*w*), (*y*), and the tapered burette end.

It will, of course, be necessary to specify diameters in ordering replacement parts. The apparatus maker should standardize these parts as well as other relevant dimensions throughout the apparatus.

There is some advantage in sealing cock 1 directly to the burette. This, of course, makes it necessary to cut off the stopcock if the burette is to be removed from the jacket. Since the burette is easily cleaned in place it will ordinarily not have to be removed. If this should become necessary, the glass blowing involved is not beyond the ability of the average amateur.

The water jacket is best made from Pyrex tubing. The outlet (*v*) which is constricted to support the compensator as previously noted, terminates in stopcock *16* which may be used to drain the jacket or admit air to stir the water.

6. THE DISTRIBUTOR

The distributor or manifold connecting the burette to the various pipettes may be filled with a confining fluid or an inert gas. A mercury-filled distributor possesses the advantage of eliminating

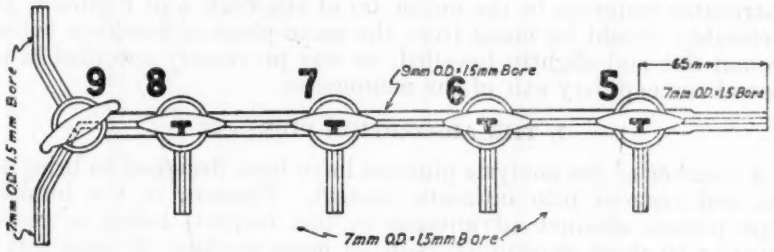

FIGURE 8.—*The distributor*

Tolerance on outside diameter of 7 mm capillary tubing, ±0.2 mm.
Tolerance on bore of all capillary tubing, ±0.1 mm.
Length of barrels of all stopcocks, 33 to 35 mm.
Diameter of keys of stopcocks, at center, 12.5 to 13 mm.
Ends of vertical leads and of left-hand horizontal outlet to be ground flat and slightly beveled at the outer rim.

errors arising from diffusion into capillary dead spaces, but such a system may trap gas unless carefully made, and, in addition, requires a relatively complicated apparatus and more skill to operate. Furthermore, it is possible to eliminate errors associated with the dead capillary space of a gas-filled train.

The usual nitrogen filled distributor has been selected, since it is better adapted to the work expected from this type of apparatus. This is shown in Figure 8. A series of tee stopcocks (*5* to *8*, inclusive) permits the gas stream from the burette to be confined to only that portion of the distributor which leads directly to the pipette into which the gas is to be introduced. This eliminates to a large extent capillary dead spaces. A 120° cock (*9*) placed at the end of the distributor permits connection to the atmosphere, an auxiliary source of nitrogen, or acidulated water if the distributor is to be

flushed in situ. The latter technique is somewhat objectionable. It becomes necessary only when a reagent is accidentally discharged into the distributor, a catastrophe which may easily be avoided when the pressure control already described is used. And in the event the operator inadvertently brings this calamity upon himself, the distributor should be dismounted and properly cleaned. Flushing in situ is at best an expedient to be used only in special cases. An alkaline reagent will ruin the grinding of the distributor stopcocks and should be washed out immediately. It is also obvious that even traces of a reagent in the distributor will spoil an analysis.

The distributor may have as many tee stopcocks as the type of analysis demands. The one illustrated in Figure 8 provides connections to pipettes containing solutions of potassium hydroxide and alkaline pyrogallol, a combustion pipette, and a fourth pipette which may be used for an additional reagent or the storage of nitrogen. As will be pointed out later on, this simple combination can be used to analyze a large number of gas mixtures.

The bores of the stopcocks and distributor are important. These are made as small as possible without introducing the danger of periodically plugging the bores with lubricant. The outside diameters are also important, and it will be noted that the distributor is stronger than the usual type. The dimensional tolerances given in Figures 8 and 1 may seem severe, but they have resulted from long and not always happy experience. The right-hand exit of the distributor connects to the outlet (*c*) of stopcock *4* of Figure 1, and preferably should be made from the same piece of capillary tubing, ground flat and slightly bevelled, as was previously specified in the case of the capillary exit of the manometer.

7. THE ABSORPTION PIPETTES

A number of gas analysis pipettes have been designed to bring the gas and reagent into intimate contact. Pipettes of the bubbling type possess distinct advantages in this respect, being in general superior to those depending upon an inner packing of some sort to provide contact surface. The ordinary bubbling pipette was first designed by Hankus in 1899.[7] It appears at present in various modifications and under various names.

A simple form of this pipette is used with the present apparatus to absorb carbon dioxide. The absorption of this gas by a solution of potassium hydroxide is very rapid, and a more complicated form of pipette is not warranted. The pipette is shown in Figure 9 (P_2). The tip of the gas inlet has been lipped to aid the emerging gas bubble in breaking away from the glass exit tube. This results in the formation of somewhat smaller bubbles. In withdrawing the gas from the pipette, the reagent is brought to etched marks shown on the capillary tubes.

The simple bubbling pipette is not as satisfactory for the absorption of oxygen. The reagent used for the absorption of oxygen is an alkaline pyrogallol solution similar to the formula recommended by Anderson.[8] Other reagents, some of them more rapid in their rate of reaction, have been tried, but these have proved to be unsatisfactory. For the quantitative removal of oxygen the pyrogallol

[7] Hankus, E. E., Osterr. Chem. Ztg., **47**, p. 81; 1899. Also J. Gasbel., **49**, p. 367; 1906.
[8] Anderson, R. P., Ind. Eng. Chem., **7**, p. 588; 1915.

solution seems to be the most suitable. The reaction is comparatively slow, and it requires about 10 passages through the plain bubbling pipette to remove oxygen from air. A more efficient pipette is therefore needed for this purpose.

Among the modifications of the plain bubbling pipette is one adapted from the Friedrichs gas washing bottle. This is described by L. M. Dennis,[9] who reports the complete removal of oxygen from air after three passages into alkaline pyrogallol contained in this form of

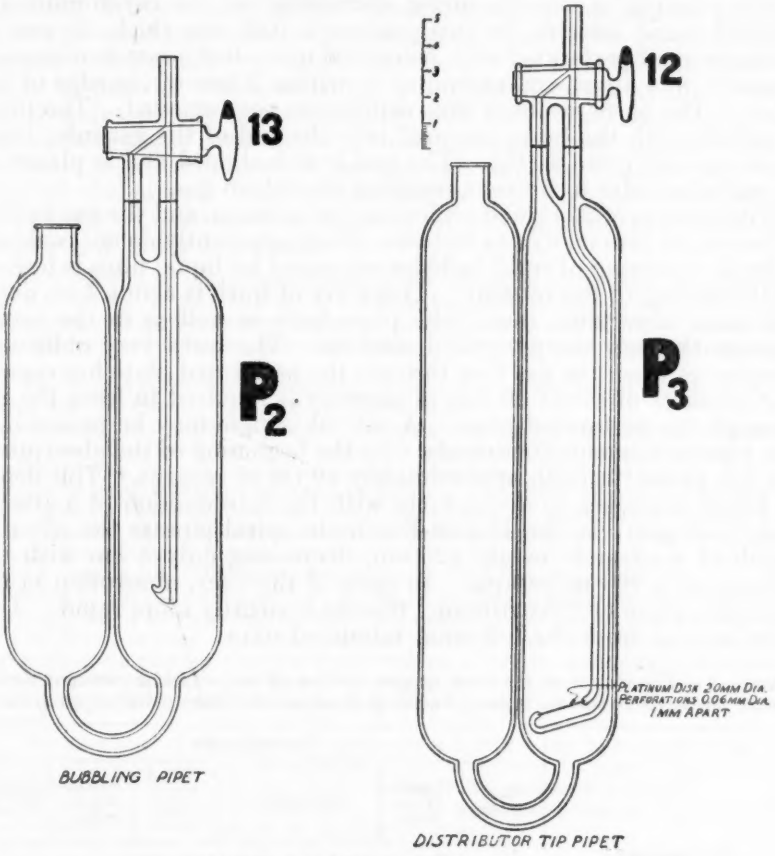

FIGURE 9.—*The absorption pipettes*

The plain bubbling pipette for less difficult absorptions is shown on the left, and the "distributor" pipette for difficult absorptions is shown on the right. The etch marks on the capillary stems are 15 mm below the bottom of the stopcock. The capillary outlet should be ground flat and slightly beveled at the outer rim. Length of barrel of stopcock, 35 mm. Diameter of key of stopcock, 12.5 to 13 mm at center. Capillary bores, 2 to 2.5 mm.

pipette. Dennis also reports a similar efficiency for the spiral pipette designed by Nowicki [10] and improved by Heinz.[11] Either of these two pipettes is satisfactory for the removal of oxygen, provided it is properly constructed. Some faults likely to occur in the construction are pointed out in a previous publication.[12]

[9] Dennis, L. M., Gas Analysis, p. 81 (fig. 47), The Macmillan Co., New York; 1913.
[10] Nowicki, Osterr. Z., Berg Hüttenw., **53**, p. 337; 1905.
[11] Heinz, J. Gasbel., p. **49**, 367; 1906.
[12] Shepherd, Martin, A Gas Analysis Pipette for Difficult Absorptions, B. S. Jour. Research, **4**, 747; 1930.

In this same note the development of a very efficient pipette is reported. The development was initiated when the Jena glass sintered filters were first introduced. The gas inlet tube of an ordinary bubbling pipette was tipped with a coarse Jena filter. The gas stream was finely divided and fairly rapid absorption resulted; but the filter plate trapped a measureable amount of gas. Accordingly, a thin platinum plate perforated with numerous small holes was substituted. Such a plate is best obtained from one of the companies engaged in manufacturing spinnerets for the rayon industry. A plate found suitable for this purpose is 0.05 mm thick, 20 mm in diameter, and perforated with holes 0.06 mm ± 0.005 mm in diameter, spaced 1 mm apart, and extending to within 2 mm of the edge of the plate. The burrs resulting from drilling are not removed. The plate is sealed (with the burrs upward) into the end of the gas inlet tube, as shown in Figure 9 (P_3). The end is dish-shaped and is placed at an angle in order to prevent trapping the return gas.

There are over 200 small orifices in such a plate, and the gas issuing is broken up into many fine bubbles, which apparently do not coalesce. A froth consisting of small bubbles separated by liquid films is formed at the surface of the reagent. This layer of froth is about 2 cm deep, and some absorption must take place here as well as in the actual passage through the pyrogallol solution. The froth very obligingly disappears when the gas flow through the perforated plate has ceased.

A pressure of about 30 mm of mercury is required to force the gas through the perforated plate. A 100 ml sample may be passed into the pipette in about 20 seconds. At the beginning of the absorption, the gas passes through approximately 19 cm of reagent. This depth of liquid decreases to about 6 cm with the introduction of a 100 ml sample of gas. In the Dennis-Friedrichs spiral pipette the effective depth of reagent is nearly 125 cm, decreasing only 5 cm with the passage of a 100 ml sample. In spite of this fact, absorption in the platinum plate or "distributor" pipette is slightly more rapid. This may be seen from the following tabulated data:

TABLE 1.—*Percentage of the total oxygen content of air which is removed during each passage into various types of bubbling pipettes containing alkaline pyrogallol*

No. of passages	Type of pipette						
	Plain bubbling	Dennis-Friedrichs	Distributor		United States Steel Co.[1 2]	Dennis-Friedrichs [1]	Nowicki-Heinz [1]
	Time consumed for each passage (seconds)						
	20	45	20	45	60	60	60
	Oxygen removed						
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
1	40.2	93.6	94.9	97.1	43.1	89.0	98.6
2	63.8	99.4	99.8	100.0	68.0	97.6	99.5
3	76.8	100.0	100.0	----	82.3	100.0	100.0
4	86.5	----	----	----	90.0	----	----
5	91.8	----	----	----	94.8	----	----
6	94.8	----	----	----	97.7	----	----
7	97.2	----	----	----	98.6	----	----
8	98.6	----	----	----	100.0	----	----
9	99.6	----	----	----	----	----	----
10	100.0	----	----	----	----	----	----

[1] Results obtained by L. M. Dennis, Gas Analysis, p. 82, The Macmillan Co., New York, 1913.
[2] A plain bubbling pipette of slightly greater length than the one shown in fig. 9.

The absorption pipettes of the apparatus are, therefore, not alike. Each pipette is designed for its specific purpose. It would be a needless expense to use the distributor pipette for the absorption of carbon dioxide and a waste of time to use the plain pipette for the absorption of oxygen. The difference in length of the pipettes is easily provided for in the supporting frame.

8. THE COMBUSTION PIPETTE

In 1920 Weaver and Ledig [13] described a new combustion pipette which possessed marked advantages and eliminated the unsatisfactory features of the usual type in general use at that time and, it must be added, at present. This usual type, originally known as the Dennis and Hopkins pipette and appearing now under various names, has two leads brought into the bottom of the pipette through a rubber stopper, whence they project through the confining fluid to near the dome of the pipette, there connecting to the platinum combustion spiral. The unsatisfactory features of this pipette are listed by Weaver and Ledig as follows:

1. It is difficult to make the stopper at the bottom of the pipette and the connections through it perfectly tight. The leakage of mercury is easily detected, but the pipette may be tight to mercury and allow air to leak in when its contents are under reduced pressure, and such a leak is likely to be overlooked for a long time.
2. The weight of the mercury in such a pipette produces a serious danger of its forcing out the stopper and spilling the mercury.
3. In order to insulate the leads it is necessary to inclose one or both of them in glass tubes. The platinum wire is usually sealed through these tubes and the connection with the lead made inside the glass tube. This is a rather difficult form of construction and one hard to repair. The point at which the wire is sealed through the insulating tube is the most likely to crack in the whole apparatus, and such cracking is likely to cause an undetected leak. If the leads pass through the glass and the active wire is crimped on, as is sometimes done, the junction usually has the highest resistance of any part of the circuit and is the first to fail in use. A solder can not, of course, be used in the presence of mercury. As the apparatus is frequently constructed, sufficient relative motion between the leads to distort or even break the platinum wire is possible. (It may be added that in case the platinum wire is supported on a ceramic body, uneven heating is apt to result and only a portion of the wire may be heated sufficiently to cause combustion to take place. Also, gas may be trapped or absorbed by the ceramic support.)
4. The necessity of bringing two leads and a tube for the flow of the confining fluid out at the bottom of the pipette makes it difficult to support so heavy a weight without mounting it on a more or less bulky supporting frame.
5. In order to replace the platinum wire it is always necessary to drain the pipette completely and usually to disconnect it entirely.

The pipette designed by Weaver and Ledig overcomes these difficulties. It is shown in Figure 10. It is made of Pyrex glass, has a volume of approximately 150 ml and is used with mercury as a confining fluid. The platinum combustion coil is strung through two side arms which are tapered slightly at the ends. Weaver and Ledig fitted soft glass caps to the outside of this taper. Through the end of each cap a heavy platinum wire was sealed. Steel caps have now been substituted (Z, Z) terminating in ordinary binding posts. These caps are not susceptible to the breakage which may occur on warming or mishandling the soft glass caps, and afford a nice means of securing the power leads to the pipette.

[13] E. R. Weaver and P. G. Ledig, New Forms of Combustion Apparatus for Use in Gas Analysis, J. Ind. Eng. Chem., **12**, p. 368; 1920.

To place the combustion coil within the pipette and secure it is a perfectly simple operation, requiring but a few minutes time. About 20 turns of the platinum wire are wound snugly around a stiff wire of approximately 1.5 mm diameter. About 8 cm of wire is left at each end of the coil. The coil is removed from the form upon which it was wound, and one of the projecting wires is bent slightly. The whole may now be easily strung through the side arms, leaving the uncoiled ends projecting therefrom. These are grasped between two fingers of each hand and the coil is stretched until it just extends across the dome of the pipette. The ends projecting from the side arms are now bent sharply upward around these arms. This holds the coil in place until the caps are slipped over the tapered ends of the side arms. The caps are cemented in place with DeKhotinsky cement. If it becomes necessary to replace the coil, one has simply to warm the caps, remove them, thread through a new coil, replace the caps, and again warm them gently to secure the DeKhotinsky seal.

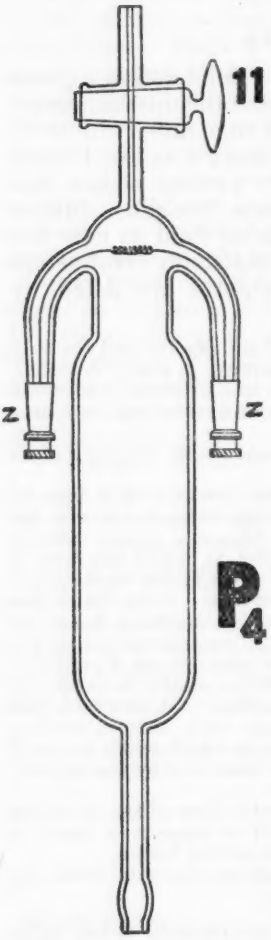

FIGURE 10.—*The combustion pipette*

Capacity, 150 ml.
Outside diameter of large section, 38 mm.
Outside diameter of top section, 26 mm.
Made from Pyrex glass.

About 20 cm of wire is required to make the combustion coil. A 90 per cent platinum-10 per cent iridium alloy is used. The diameter of the wire should be 0.16 to 0.17 mm. Wire of this size will make a coil which supports itself at white heat, and the current required to heat it is not excessive. (About 2 to 2.3 amperes. The ordinary 110-volt circuit is used in connection with a tubular rheostat rated at 120 ohms, 2.2 amperes.)

When the pipette is first filled, mercury falls into the side arms and makes the electric contact between the caps and the combustion coil. These arms are of sufficient length to dissipate the heat from the dome of the pipette, so that the cement is not softened.

This pipette has been found so much more satisfactory than the usual type that the latter has been entirely abandoned in our laboratories.

No provision has been made for connecting a fractional combustion tube. When the apparatus is made, additional tee cocks placed one on each side of the cock which connects the combustion pipette to the distributor (cock 7 of fig. 8) with the outlets pointing upward, will accommodate such a tube. Its use is left to the judgment of the analyst.

9. THE SAMPLING PIPETTE

The sampling pipette used is similar to the standard type constructed with two so-called "3-way" stopcocks, as shown in Figure 11. The convenience of this arrangement is at once apparent. The sampling line may be flushed with the sample itself or with a confining fluid when the sample is taken. Similarly, the same operations may be performed after the pipette is connected to the burette. And, finally, air may be displaced from the tubing connecting the leveling bulb containing the displacing fluid. The identity of the sample is thus preserved at all times and with no extra trouble.

The capillary exits at the top and bottom are of different bores, and are designed to accommodate the flow of gas (top) and confining fluid (bottom). The capacity of the pipette is large enough to provide three samples for analysis.

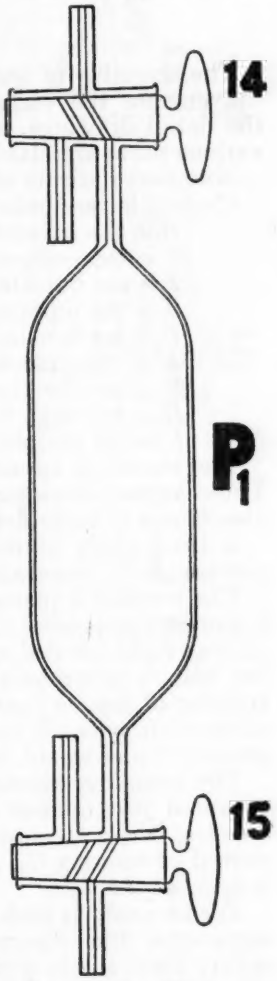

FIGURE 11.—*The sampling pipette*

Capillary tubing of stopcock *14*, 7 mm o. d. x 1.5 mm i. d.
Tubing of stopcock *15*, 7 mm o. d. x 4 mm i. d.
Length of bulbed portion, 150 to 155 mm.
Over-all length, 290 mm.
Capacity, 2-sample size, 220 ml.
Capacity, 3-sample size, 330 ml.

10. METHOD OF SECURING CONNECTIONS

The connections between the distributor and the pipettes and burette, and between the burette and manometer, are made with rubber tubing. In view of the fact that the pressures within the apparatus do not differ greatly from atmospheric, this simple method is satisfactory. The rubber connection, however, should be properly secured. A simple and very effective method for doing this is as follows: The ends of the capillary tubes are butted as closely together as possible. The joint is then secured by wrapping a number of turns of heavily waxed dental floss around the rubber tubing above and below the point at which the glass capillaries meet. Each turn is pulled tight and the wax upon the silk floss holds each turn in place until the next one is made. A connection properly made in this manner will not leak under the ordinary pressure conditions existing during the analysis. The bore of the rubber tubing should be a little, but not much, smaller than the outside diameter of the glass, so that the rubber will be under compression beneath the wrapping and under only slight tension elsewhere.

If a suitable grade of transparent gum tubing is available, its use is to be preferred, largely on account of the desirability of observing the mercury thread in the capillary exit of the manometer when the gas in this arm of the manometer is displaced. The rubber tubing should be replaced frequently enough to keep it in good condition,

since old rubber tubing is a prolific and frequently unsuspected source of leaks.

Sulphur-free rubber tubing should be used to connect L_1 to B, L_2 to P_1 and L_3 to P_4. Nitrometer tubing of reddish-gray rubber, which will not foul mercury, has been found best.

11. THE ASSEMBLY

The assembly of the gas analysis unit is shown in Figure 12. For convenience the various parts have been lettered to correspond to the detail drawings which have preceded. The designations of the various parts are classified as follows:

Numbers indicate stopcocks.

Capital letters indicate major parts of the apparatus:

B is the burette.
C is the compensator.
I is the burette illuminator.
J is the burette water jacket.
L_{1-3} are leveling bulbs.
M is the manometer.
P_{1-5} are the pipettes.
R_{1-7} are rings which support the leveling bulbs.
S is the sampling connector.

The electrical apparatus and circuits are not shown in Figure 12. These appear elsewhere in a photograph. The apparatus support is also shown in more detail in this photograph and a drawing.

A brief study of the assembly drawing will afford a preliminary picture of the apparatus as a unit.

The burette is placed at the right so that the manipulation of the important stopcocks *1*, *2*, *3*, and *4* and the leveling bulb L_1, is natural to a right-handed operator. It will be remembered that the leveling bulb is never held in the hand during a pressure adjustment or transfer of gas, so that its manipulation does not interfere with that of the stopcocks. If the operator is left handed, a mirror image of the present model would be more suitable for his use.

The sampling pipette P_1, which is a nomadic part of the unit, is mounted just outside of the frame proper and to the right of the burette, where a connection is easily made. Its leveling bulb is supported on the ring R_5, which is mounted on the back of the frame and is open at the side.

For an analysis such as will be described to illustrate the use of the apparatus, the absorption pipettes are arranged in the following order: First is the pipette P_2 containing potassium hydroxide solution. Next is P_3 containing alkaline pyrogallol. Following this is the combustion pipette P_4. And finally the absorption pipette P_5, which is used as a source of nitrogen for the distributor. This system of pipettes is arranged to correspond to the various steps of the analysis. The combination is reduced to as simple a form as possible for ordinary gas analysis, and may be elaborated to suit special requirements.

The leveling bulb L_3 connected to the combustion pipette is supported on the rings R_6 and R_7, which are open at the side and mounted

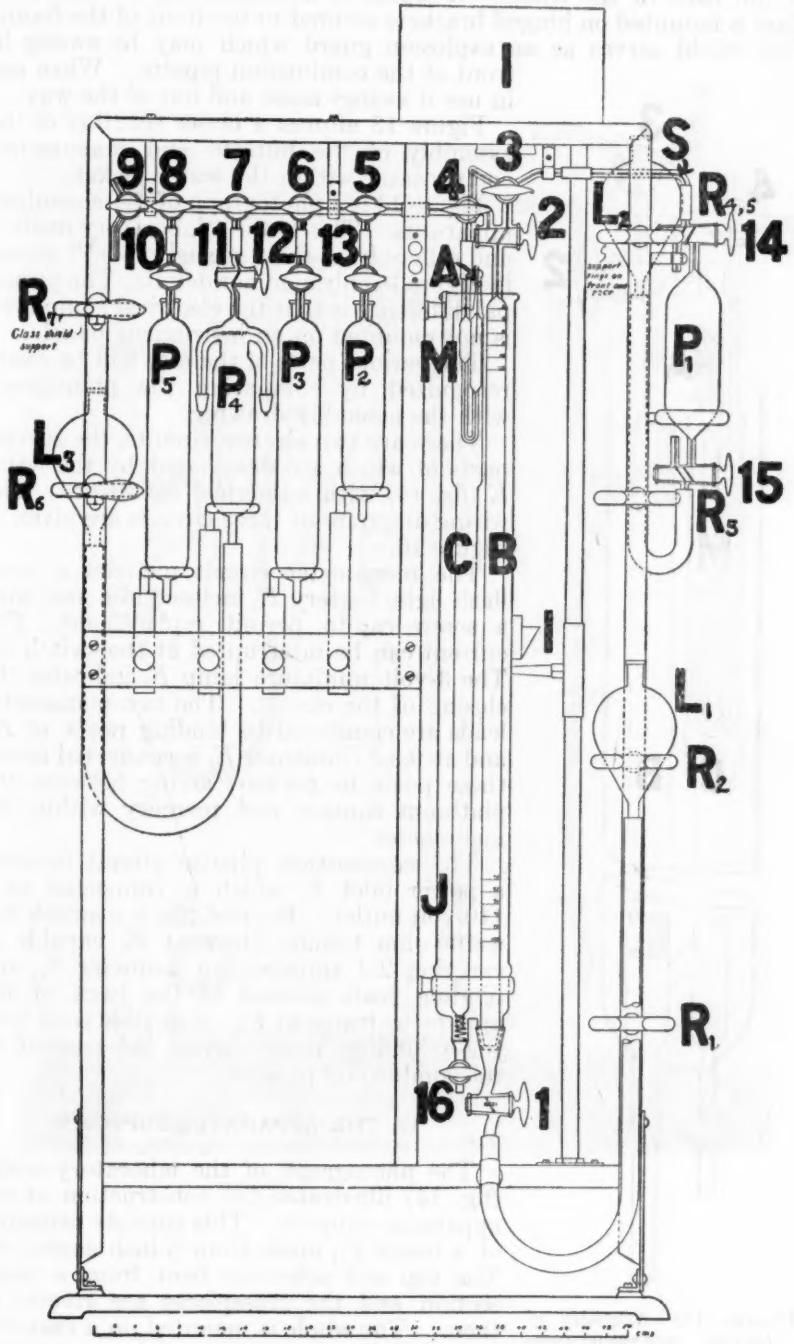

FIGURE 12.—*The assembled apparatus*

at the back of the frame. A shield of nonshattering or laminated glass is mounted on hinged brackets secured to the front of the frame. This shield serves as an explosion guard which may be swung in front of the combustion pipette. When not in use it swings aside and out of the way.

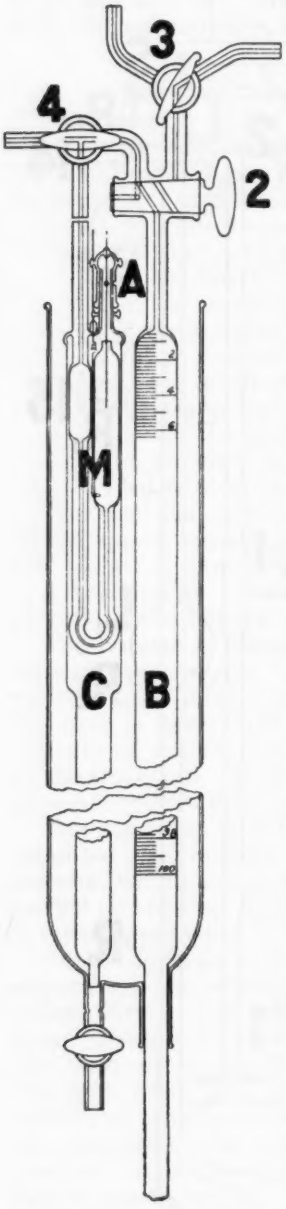

FIGURE 13.—*Assembly of burette, manometer-compensator, and water jacket*

Figure 13 affords a closer scrutiny of the assembly of the burette and manometer-compensator within the water jacket.

Figure 14 is a photograph of the assembled apparatus. This is the "laboratory model" and differs from the "special model" shown in Figure 15 only in minor details. The principal difference is that the electrical equipment is not mounted on an instrument panel.

The various parts of the unit will be easily recognized by comparing the photograph with the assembly drawing.

There are two electric circuits, the several parts of which are designated by the letter E (fig. 14) with numerical subscripts. The wiring diagrams of these circuits are given in Figure 16.

The manometer circuit includes a 3-cell flash light battery E_5 inclosed in a case with a screw cap to permit replacement. The current can be interrupted at the switch E_4. The 3-volt miniature lamp E_2 indicates the closing of the circuit. The two manometer leads are connected to binding posts at E_1, and at 0.5μf condenser E_3 is connected across these posts to prevent arcing between the platinum contact and mercury within the manometer.

The combustion pipette circuit includes a power inlet E_9 which is connected to a 110-volt outlet. Beyond this is a switch E_{10}, a 100-ohm tubular rheostat E_8 capable of carrying 2.2 amperes, an ammeter E_7, and binding posts located at the back of the apparatus frame at E_6. A flexible cord from these binding posts carries the current to the combustion pipette.

12. THE APPARATUS SUPPORT

The photograph of the laboratory model (fig. 14) illustrates the construction of the apparatus support. This consists primarily of a frame F_1, made from ¾-inch angle iron. The top and sides are bent from a single section and the crosspieces are riveted to them. The whole is mounted on a cast-iron base F_5. The crosspieces and gusset plates

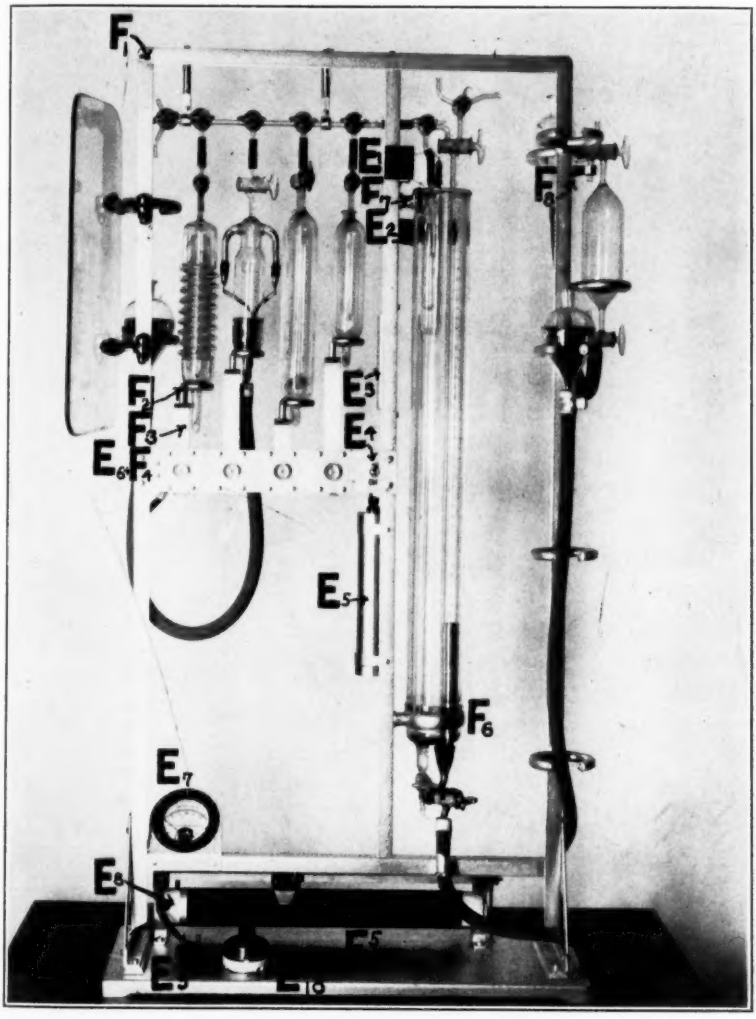

FIGURE 14.—*The laboratory model*

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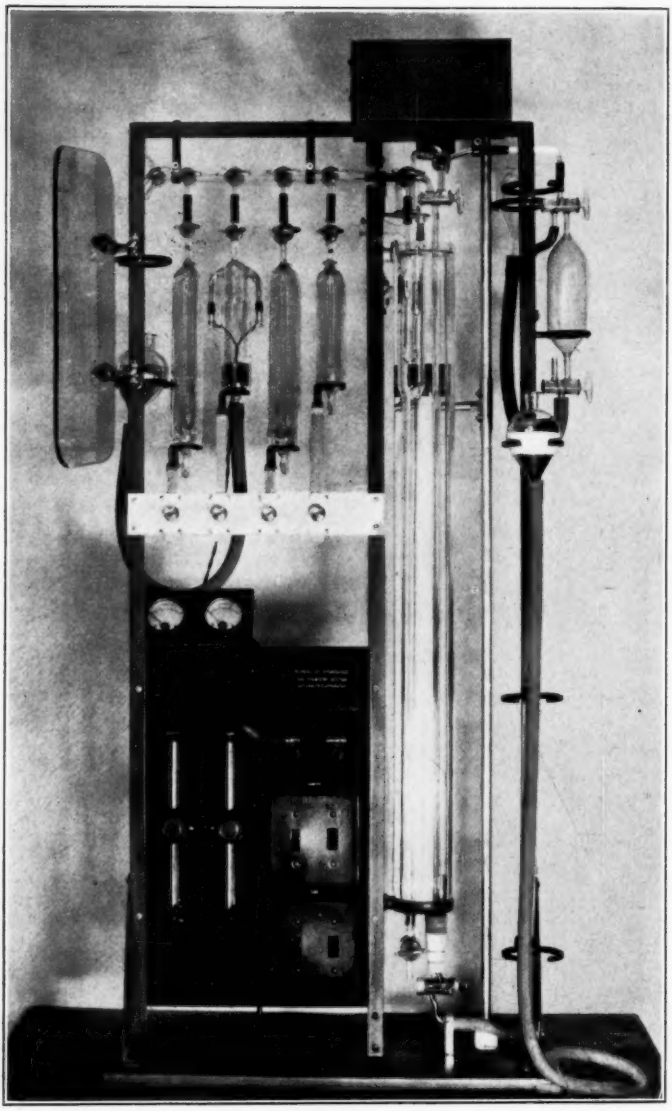

FIGURE 15.—*The special model*

at the bottom insure the necessary rigidity. This type of support is superior to the usual wooden mounting. It is free from warping and makes the apparatus much more accessible.

The water jacket rests in the ring F_6 and is secured at the top by two friction clips F_7. The sampling pipette rests on a split ring and is held at the top by a friction clamp F_8. The absorption and combustion pipettes rest on split rings F_2, which are mounted on sliding supports F_3 secured to the crossbar F_4.

A detail drawing of the pipette support is given in Figure 17. The rings are secured to the sliding supports by machine screws, and are, therefore, adjustable to accommodate pipettes of various widths. The sliding supports are guided by the grooved pieces F_9 and secured in place by the set screws F_{10}. The spacers F_{11} fix the crossbar F_4 at the proper distance outward from the frame, so that the pipettes may be connected to the distributor without off-set. The whole pipette support is chromium plated.

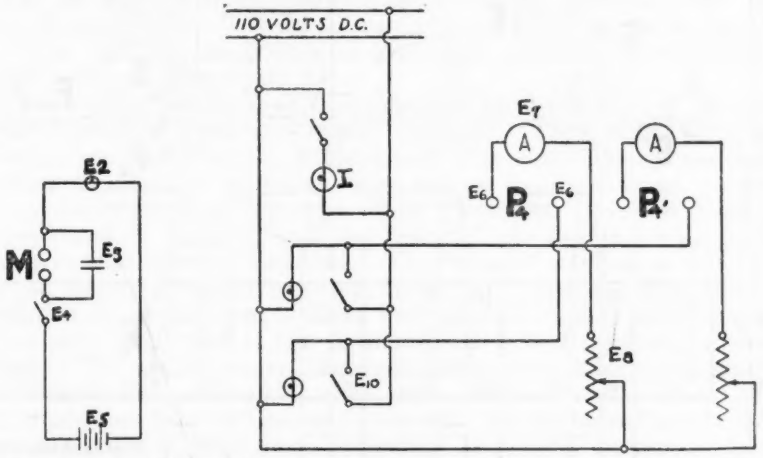

FIGURE 16.—*Wiring diagrams for the manometer and combustion pipette circuits*

The 3-volt manometer circuit is shown at the left. The 110-volt circuit shown at the right provides connections to two combustion spirals with pilot lights in each circuit, and also provides current for the burette lamp.

The apparatus support is designed to permit the removal of any part of the apparatus without disturbing other parts. The glass parts are so easily accessible that it is possible to completely assemble or dismount the apparatus in a few minutes.

13. STOPCOCKS

It is very important that only the finest stopcocks be used in the construction of the apparatus. The stopcocks ordinarily supplied are not satisfactory. While no high vacua obtain within the apparatus, stopcocks suitable for this kind of work should be used. This does not imply a mercury seal, but rather specifies the finest grade of grinding, which is often referred to as the "mirror finish." The bores of key and barrel should register and be free from chipping.

When the stopcock is properly lubricated there should be no bubbles, films, or streaks of air between the surfaces of key and barrel. A satisfactory lubricant is the general grade described by Shepherd

and Ledig.[14] A technique of lubrication is also given in the same paper. The reader may find the details given in this paper of some value. An abstract is given in the following paragraphs:

The general lubricant is made from—	Parts
Rubber (pale crêpe, freshly milled, free from all dirt and lint)	6
Vaseline	7
Paraffin (m. p. about 40° to 45° C.)	1

The vaseline and paraffin are melted in a large porcelain casserole, and the rubber is added in several portions. The mixture is placed in a thermostated oven and stirred continuously for 190 hours at 155° to 160° C. It is then transferred to 2-ounce ointment cans and chilled on ice immediately, care being taken to prevent the condensation of water in the lubricant.

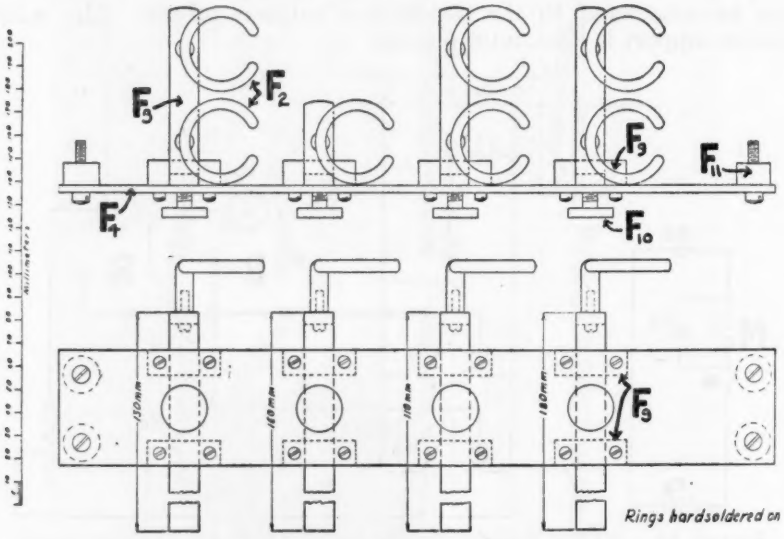

FIGURE 17.—*The pipette support*

There are many methods of lubricating a stopcock, and not all are entirely satisfactory. A method familiar to many acquainted with high-vacuum technique may be recommended. The lubricant is applied in two parallel longitudinal streaks, one on either side of the key and away from the bore. The streaks should be as thin as possible, and contain only enough lubricant to flow entirely around the key. The lubricant so placed, the key is held above a soft Bunsen flame, so that the grease just melts to form a smooth ridge of approximately semicircular cross section. The key is allowed to cool and then carefully inserted into the barrel so that the bores of key and barrel coincide. The key is pressed downward into place, with little, if any, turning, the lubricant forming V's on either side of the bore

[14] Rubber Stopcock Lubricants for High Vacuum and Other Uses, Ind. Eng. Chem., **9**, p. 1059; 1927.

and pressing out all air films until it has flowed smoothly around the entire grinding.

The stopcock key should never be turned with a spasmodic jerk, but rather should be rotated with a slow, smooth motion.

IV. METHODS OF ANALYSIS AND TECHNIQUE OF OPERATION

The portion of the following section which deals with the actual technique of operation is written largely for the benefit of the inexperienced operator and also for the analyst who has been accustomed to using the ordinary commercial types of apparatus. It is intended to give the instructions in sufficient detail so that a clear understanding of the manipulative processes will be obtained, and a great deal of trouble avoided. Several advantages of the apparatus are brought out during the discussion of the operating technique, and the methods given for making exact analyses are somewhat different from those usually employed. The detail may prove a bit tiresome to one more familiar with gas analysis, and from such a reader consideration is asked where it is required.

It is well to point out at this time just what is meant in this paper by a "technical" and an "exact" analysis. These terms have been used in textbooks on the subject and have consequently assumed a certain significance to which they are no doubt entitled, provided everyone knows what is meant. The "technical" analysis is a rough approximation to truth and the "exact" analysis is a step further along in that general direction. The "exact" analysis is not exact, but is merely designed to catch up some of the loose threads of the technical effort and weave them into a fabric that is still in need of some patching before it can be made into a totally presentable garment. The usual "exact" analysis is actually a technical analysis performed with somewhat more than ordinary care. The field of exact analysis has not been well covered. So far there have been but few explorers in this more difficultly accessible territory. In the present paper, the term exact analysis has been misused to partially conform to general practice, although it is hoped that the analyses to be achieved under this classification may be somewhat more accurate than are usually reported as "exact." And certainly the technical analyses spoken of herein should be of a better grade than those generally performed under that name—perhaps the equal of many so-called "exact analyses."

1. SAMPLING

A great deal has been said concerning various methods of taking the gas sample. Special conditions often obtain and may require other than the routine technique. It is beyond the scope of the present paper to report the rather ingenious methods devised to meet these unusual cases. It will be assumed that the sample is readily accessible.

The important fact is this: The analysis can be no better than the sample. This simple fact has been stated repeatedly—and as repeatedly ignored. The analyst has only to ask himself: "Is this the gas that will tell me the story I must know?" And not until the

question is given an affirmative should the sample be taken. (The attention of the engineer is also respectfully referred to that question.) Two questions follow this: "Is the sample secured within the container identical with the gas drawn from the source of supply?" And, finally: "Is the sample transferred to the analytical apparatus of exactly the same composition as the gas within the sampling container?"

A pair of honest affirmatives to the last questions may be claimed by observing simple precautions. The stopcocks of the sampling pipette (P_1) must be trustworthy. This means that they have been carefully ground to a "mirror" finish, as have all of the stopcocks of the analytical apparatus; and that they have been properly lubricated.[15]

The leveling bulb L_2 (fig. 12) is connected to the lower outlet of cock *15* of the sampling pipette, and the pipette is then filled with clean mercury. A tube of small bore and minimum length is connected to the source of the sample and to the upper outlet of cock *14*. This sampling line is then flushed with gas from the source of supply by turning cock *14* to connect the line to the atmospheric outlet of *14*. The stopcock is then turned to connect the source to the pipette, and the sample is taken in over mercury. If the gas at the source is not under pressure, a 120° stopcock similar to cock *3* of the burette is connected to the upper outlet of *14*, and the sampling line is connected to one of the two free outlets of this additional cock. A sample is then drawn into the pipette by lowering L_2, and this gas is expelled, without disconnecting the sampling line, through the third or atmospheric outlet of the 120° cock. Air which was originally in the sampling line is thus displaced, and a fresh sample may now be taken for analysis. If an aspirator is available, it may be connected to the atmospheric outlet of *14* and the sampling line flushed by drawing gas through the aspirator.

The sample should be taken under slight pressure whenever possible. When rubber connections are used they should be secured with waxed floss in the manner previously described, unless the sampling conditions permit the maintenance of a positive pressure within the system at all times. The sample should be left in the pipette under pressure, and should be analyzed as soon as possible after it is taken.

The sampling pipette is mounted on the apparatus support as shown in Figure 12. If the pipette has been disconnected from the leveling bulb L_2 in transferring it to the apparatus, it will be necessary to displace air from the tube connecting L_2. This is done by opening cock *15* to its atmospheric outlet and allowing mercury from L_2 to flow slowly upward through the bore of the cock. Similarly, air contained in the capillary sampling connection S is displaced by mercury from the burette. The mercury is allowed to drain from the atmospheric outlet of *14* and may be caught in a rubber tube leading to a beaker, or a steel tube may be mounted onto the frame in such a way as to act as a mercury drain and a support for the atmospheric outlet of *14*. The latter arrangement is pictured in the photograph of the special model. (Fig. 15.)

If this technique is carefully followed, the sample entering the burette should be identical with the sample drawn from its source of supply.

2. PREPARATION OF THE APPARATUS FOR AN ANALYSIS

(Refer to fig. 12 unless otherwise specified)

Burette, manometer, and compensator.—The burette and manometer should be cleaned with sulphuric-chromic acid before they are mounted on the frame. The compensator must contain a few milliliters of water. The manometer is dried and very clean mercury is introduced with the ground cap A removed. The amount of mercury in the manometer should be sufficient to bring the meniscus within approximately 0.5 mm of the platinum contact (n) (fig. 4) when the manometer is leveled and both arms are at atmospheric

[15] See footnote 14, p. 142.

pressure. The leveling bulb L_1 should contain enough clean mercury to completely fill the burette and leave an excess within the bulb. All air bubbles, which may be in the rubber tubing connecting the bulb with the burette, must be displaced by mercury flow.

Absorption pipettes.—For the sake of completeness, the preparation of the reagents used in the illustrated analysis may be described. The reagent used for the removal of carbon dioxide in the absorption pipette P_2 is a potassium hydroxide solution. This is prepared from a solution of potassium hydroxide in water (800 g KOH per 1,000 ml of solution) which is then cooled to a temperature several degrees lower than will exist where the apparatus is used. The clear solution decanted from the deposit of carbonate and excess potassium hydroxide is satisfactorily pure and will not deposit solid within the pipette. Its specific gravity should be approximately 1.55 at 20° C. It may be used for making up both the KOH and KOH-pyro solutions. For the absorption of carbon dioxide in the pipette P_2, this solution is diluted by adding 50 to 60 ml of water to each 100 ml of concentrated potassium hydroxide solution.

The reagent used for the removal of oxygen in the absorption pipette P_3 is an alkaline pyrogallol solution. This is made by dissolving crystalline pyrogallol in a minimum amount of hot water and adding this solution to the concentrated potassium hydroxide solution as prepared above. Fifteen to seventeen grams of the pyrogallic acid dissolved in about 5 to 10 ml of hot water is added to each 100 ml of the concentrated potassium hydroxide solution in the manner decribed below. The resulting solution closely approximates the one recommended by Anderson,[16] who found a solution containing 15 g of pyrogallol per 100 ml of potassium hydroxide solution of 1.55 specific gravity to be satisfactory. Anderson observed foaming in a reagent containing more than 15 g of pyrogallol/100 ml of solution, but this apparently does not occur in a pipette of the type of P_3 when 17 g of pyrogallol/100 ml of solution is used.

In order to prevent air from reaching the reagents a layer of light mineral oil, about 10 to 15 mm in depth, is poured over the reagent in the reservoir arm of the pipette. This also permits the preparation of the pyrogallol solution within the pipette itself and out of contact with air. The potassium hydroxide solution is first introduced, the oil is placed over this solution, and the pyrogallic acid solution in water is introduced beneath the layer of oil from a pipette. Mixing is obtained by several passages of a large volume of nitrogen from the burette to the pipette.

The amount of reagent put into the pipette should be just sufficient to completely fill the pipette without overflowing from the reservoir arm when the pipette contains 100 ml of gas. Account must also be taken of the layer of mineral oil when this maximum volume of reagent is determined.

A record should be kept of the amount of oxygen absorbed, in order that the absorbing capacity of the pyrogallol solution will not be exceeded.

The absorption pipette P_5 is ordinarily employed as a reservoir for nitrogen used in flushing the distributor, and contains alkaline pyrogallol solution. It can be used for other absorptions as these may

[16] R. P. Anderson, J. Am. Chem. Soc., **1**, p. 587; 1915.

occasionally become necessary. If such necessity is more than occasional, the distributor and apparatus should be extended to accommodate the requisite number of pipettes.

Many of the additional absorptions which may be desirable involve reactions which are apt to be conflicting or even not satisfactorily quantitative. The reagent may not be quantitatively selective, and the gas mixture may present a combination which is difficult to handle in this type of analysis. The well-known reagents are discussed by Dennis,[17] and some of their limitations are cited. The reader who is not familiar with this subject will find a good discussion given by Dennis.

Combustion pipette.—The platinum helix over which the combustion occurs is placed in the pipette in the manner previously described. The pipette is then filled with clean mercury from L_3, leaving a slight excess of mercury in this bulb. Care is taken to displace all air from the side arms of the pipette. The mercury is not allowed to flow into the bore of stopcock *11*.

Test for leaks.—When the apparatus has been assembled and all rubber connections secured with waxed floss, the stopcocks properly lubricated, and the jacket J filled with water, the apparatus should be tested for possible leaks. The average beginner using the average apparatus will experience a great deal of difficulty which is directly chargeable to this source of error. A large leak lends itself to early discovery; but a small leak may be insidious, appearing and disappearing in the final results in most perverse ways. Such sources of error are so difficult to detect that the beginner frequently confuses them with inability to master the technique. The present apparatus should improve this situation. It will be remembered that all stopcocks are made to specifications far more rigid than the average, and that a careful technique of lubrication has been prescribed, and finally that a trustworthy method of securing rubber connections has been given. The combustion pipette P_4 replaces a well-known type that is apt to cause the most serious sort of errors due to leaks whose presence may not be suspected. So little difficulty from leakage in this apparatus has been experienced that it has become of minor importance. (This is true only if the rubber connections are kept in excellent condition.)

It is always advisable to test the assembled apparatus in order to make perfectly sure that it is free from leaks.

This is done by taking a small measured volume of air into the burette, closing all stopcocks, and reducing the pressure within the burette by lowering L_1 to R_1. At the end of 15-minute intervals volume readings are taken and compared with the original volume, each stopcock being opened in turn so that the leak, if present, may be located at the termination of the particular 15-minute interval during which leakage occurred. The test is then repeated with a pressure greater than atmospheric. Volume readings are to be taken in the manner to be described in the succeeding section.

3. CONSIDERATIONS PRELIMINARY TO THE ACTUAL ANALYSIS

When the apparatus has been assembled and prepared according to the directions just given, and the sample has been taken in P_1 and transferred to the apparatus, the actual operation of analysis is begun. It will be well to go through the steps of a complete analysis, and for

[17] Dennis, Gas Analysis. The Macmillan Co., New York.

this purpose we will assume that the sample contains carbon dioxide, oxygen, methane, carbon monoxide, hydrogen, and nitrogen.

It is, of course, understood that a volume of this mixture must be measured, and that each constituent must be removed and the contraction in volume resulting from its removal must be determined. The comparison of these diminishing volumes with that of the original sample affords the basis for determining the various percentages of the components. It is therefore necessary that each volume measured be corrected to the same temperature and pressure. This is automatically accomplished by use of the manometer-compensator unit, which is a modification of the usual temperature-pressure compensation system. The compensator itself is of the same size as the burette and placed parallel to it. Both are surrounded with water. The temperature of one closely approximates the temperature of the other at all times.

The pressure in the compensator is fixed at the beginning of an analysis by closing *A*, and the pressure of the gas which is measured in the burette is always adjusted to this same fixed pressure by means of the manometer which indicates when this fixed pressure has been obtained within the burette. The gas within the burette must be saturated with water before every measurement, and the compensator contains water, so that the vapor pressure within one balances the vapor pressure within the other. The series of gas volumes which are to be compared are, therefore, converted to uniform conditions of temperature, pressure, and humidity without calculation.

Another point should be clearly understood before describing the actual steps of the analysis. It has been pointed out that the distributor connecting the parts of the apparatus is of the gas-filled type. An inert gas must be used, since no portion of this gas must react during the analysis. Nitrogen remaining after the absorption of oxygen from air is ordinarily used, since this is conveniently prepared within the apparatus itself. The pressure of the gas within the distributor must be the same as the fixed pressure of the compensator at the beginning of an analysis and at all times during the analysis when a volume is to be measured. It is obvious that if this condition did not exist, the gas volumes measured in the burette would be larger or smaller than they should be by the amount of gas drawn from the distributor at a pressure less than that of the compensator or compressed into it at a pressure greater than that of the compensator.

Water upon the burette wall.—The original sample and its various fractions are saturated with water before each volume is measured. This is done by maintaining a film of water upon the wall of the burette. The left-hand outlet of stopcock *3* is immersed in distilled water contained in a small beaker. (See fig. 15. The platform supporting this beaker swings aside to permit the removal of the beaker.) A few milliliters of water is drawn into the burette over the mercury, the mercury is lowered to the 100 ml mark, and then slowly raised, and the surplus water expelled. The wall of the burette will retain enough water to saturate the gas. No water should be left on the mercury, since this would interfere with the reading of the position of the meniscus. Since the potassium hydroxide and alkaline pyrogallol solutions both remove water from the gas, the presence of water upon the wall of the burette must be checked after the completion of each absorption. If the water is not present, serious errors will result. If

the water film disappears during the course of the analysis, it may be renewed by displacing all gas from the burette, temporarily storing the gas in the particular pipette in use at the time and again wetting the wall of the burette.

Difference in analytical procedures.—The method of supplying oxygen for the combustion will determine the actual procedure. Oxygen may be obtained by using air and multiplying the measured volume of air by 0.2095 to obtain the volume of oxygen used. Since this leaves a large volume of nitrogen which must be measured after the combustion, it is necessary to use a small sample of gas for the combustion analysis. The accuracy is accordingly decreased. For this reason many analysts prefer to use pure or nearly pure oxygen. This may be obtained from an auxiliary apparatus designed to generate and purify the gas, or from a cylinder of compressed oxygen, which has been obtained from air separation, and has been previously analyzed to determine the percentage of inert gas and establish freedom from combustible vapors.

The analytical procedure is somewhat different in the two cases, and, accordingly, will be outlined for each. The procedure undertaken for exact analysis is also different from that used for technical or approximate analysis, and the differences will be pointed out as the instructions are developed. It will be observed that an exact analysis requires many extra steps and a great deal of care and patience.

4. ANALYTICAL PROCEDURE; AIR USED FOR THE COMBUSTION

It is now assumed that the apparatus is prepared for the analysis as previously described. The pipettes are filled with reagents to the etch marks on the capillary stems, or, in the case of P_4, with mercury to the bore of stopcock *11*. The burette is filled with mercury, and the manometer is standing at approximate balance with *A* open to the atmosphere. The sample pipette is mounted in place, and contains a mixture of carbon dioxide, oxygen, methane, carbon monoxide, hydrogen, and nitrogen. We may now proceed.

Filling the distributor and manometer.—The first step is to fill the distributor and the arm of the manometer connected thereto with nitrogen at the pressure which is to be fixed within the compensator.

To do this, *2* is turned to *3*, *3* to the atmosphere, L_1 placed on R_1, and *1* is opened until about 10 ml of air has entered the burette. Cock *1* is then closed, *2* turned to the distributor, and *4* to connect the manometer. Cock *1* is now slowly opened, the mercury in the manometer arm connected to the distributor rises, and *1* is turned to the constriction as the mercury nears the bore of cock *4*. When the mercury reaches this bore, *1* is closed. The manometer is shut off by turning *4* upward. Air has now been displaced from the manometer. Cock *2* is turned to *3* and *1* opened to admit about 100 ml of air to the burette. The oxygen is now removed from this air. Cock *1* is closed, L_1 placed on R_4, and *2* turned to the distributor. (Stopcocks *4*, *5*, *6*, and *7* are turned upward.) Stopcock *8* is turned to connect P_5 and shut off the balance of the distributor to the left. Cock *1* is opened slowly, and when the volume within the burette has been compressed several milliliters, so that there is no danger of drawing reagent into the distributor, *10* is opened. Air from the burette now passes into P_5 containing alkaline pyrogallol solution, and the removal of oxygen is started.

Refer now to Figure 9. It will be seen that the handle of stopcock *10* is marked at one end to indicate the direction of gas flow. When the marked end points upward the stopcock is turned to withdraw the gas from the pipette, and conversely when the marked end points downward the stopcock is in the proper position to introduce the gas into the pipette. On the other hand, when the

sample is initially introduced into the pipette, *10* is turned upward until the reagent drains from the the left-hand capillary, and then turned downward to conduct the absorption. If this were not done, the reagent in the left-hand capillary would not drain out, and when *10* was turned upward to return the gas to the burette, the reagent trapped in this tube would immediately be drawn into the distributor, which is one of the major tragedies of gas analysis.

Three passages are sufficient to remove the oxygen. After the final passage the nitrogen is returned to the burette, the level of the reagent in the pipette being adjusted to the etch marks on the capillary stems just below stopcock *10*, after which *10* is closed, and *7* is turned to the position ⊢. It may be noted here that the alkaline pyrogallol solution is a comparatively viscous reagent, and returns slowly through the small orifices of the platinum distributing plate used in this type of absorption pipette. The ordinary technique for returning the gas from the absorption pipette to the burette is to turn the pipette stopcock upward to connect both capillaries to the burette. If the stopcock is turned downward for the return of the gas, reagent is immediately drawn up the capillary gas inlet and into the distributor. This will happen in a pipette such as P_2, but on account of the comparatively slow flow of reagent through the distributing plate (P_3 and P_5), the following technique is used. The pipette stopcock is allowed to remain in the downward position for delivery of gas to the pipette. The pressure is reduced by allowing the mercury within the burette to drop about 20 mm. The reagent then flows through the perforated plate and into the capillary within a few seconds, but rises in the capillary at an easily controlled rate. The pipette stopcock is then turned to the normal position for the return of the gas to the burette. This technique is not absolutely necessary, but will save time. The reagent is adjusted to the etch marks on the pipette capillaries by turning stopcock *1* to the constricted bore.

Nitrogen now fills all of the distributor except the capillary leads from stopcocks *5*, *6*, and *7* to stopcocks *13*, *12*, and *11*, and the spaces within the capillary stems of P_2 and P_3 above the reagents. The air inclosed in these capillary spaces must be displaced.

This is accomplished by diluting these small volumes with the large volume of nitrogen within the burette. Nitrogen is first passed from the burette to P_4, returned, and passed into P_2, returned, and then passed into P_3, where the residual oxygen is removed during one passage. The reagents are adjusted to the etch marks on the capillary stems of the pipettes P_2 and P_3, and mercury to the bore of cock *11*, as the gas is returned from each of these pipettes.

The burette is now connected to P_5 and all but about 10 ml of nitrogen is passed into this pipette for storage and future use after which *1* is closed. Cock *10* is closed, *8* turned to the position ⊢, and *7*, *6*, and *5* turned to the position ⊤.

The pressure within the distributor and manometer is now balanced against the compensator.

Stopcock *2* is closed, *1* is opened, and the pressure within the burette is adjusted to approximately that of the atmosphere by raising and lowering L_1 which is momentarily held in the hand for this purpose. A comparison of the mercury levels within *B* and *L* will indicate when the gas in *B* is under approximately atmospheric pressure. When this condition is reached, *1* is closed, L_1 placed on R_4, and *2* opened to the distributor. Cock *4* is now turned in the position ⊤, which simultaneously connects the distributor and the burette to the manometer. The mercury within the arm of the manometer connected to the distributor will fall, but not enough mercury will have been admitted to the compensator arm of the manometer to bring the meniscus here in contact with the platinum reference point. Cock *1* is now slowly turned to only partially open the full bore, whereupon mercury will approach the platinum point. Cock *1* is closed when the mercury is within approximately 1 mm from this point. *A* is now closed, thus shutting off the compensator and fixing the pressure therein. *A* is not touched during the remainder of the analysis, and all gas volumes are measured by comparison with the fixed compensator pressure. Cock *1* is now opened to the constriction. The mercury within the compensator arm of the manometer will now flow very slowly upward until it touches the platinum point. At the instant when the 3-volt circuit is closed, and the miniature lamp flashes on, *1* is closed.

All other pressure adjustments are made in this manner, except that, of course, *A* is not turned, and the control cock *1* is turned

from the partially opened full bore to the constricted bore and then closed, rather than being closed before turning to the constricted bore as was necessary above. The end point is always obtained with the mercury rising toward the contact point, never the reverse. If for any reason the contact point is accidentally overrun, *1* is closed, L_1 lowered to a ring below the mercury within the burette, *1* carefully opened until the mercury falls below the contact point, and the operation of adjusting the pressure repeated.

The distributor and the arm of the manometer connected thereto now contain nitrogen under the fixed compensator pressure. Cock *2* is turned to *3*, and the nitrogen remaining in the burette is expelled to the atmosphere, the mercury in the burette being forced just past stopcock *3*. The apparatus is now ready for the introduction of the sample.

Introduction of the sample.—The sample pipette is connected to stopcock *3* of the burette by the capillary glass tube *S*.

Air is displaced from this line by opening *14* to the atmosphere and forcing mercury from the burette through the line. (L_2 has already been connected to *15* and the air displaced by mercury from L_2 through the atmospheric outlet of *15*.) L_2 [18] is now opened to P_1 through *15*, thus compressing the sample in P_1. Stopcock *14* is opened to the burette, stopcock *1* closed, L_1 placed on R_1, and stopcock *1* opened slowly to admit the sample to the burette. When the mercury in the burette has reached a point somewhere between the 84 and 86 ml marks, *2* and *14* are closed in the order named.

The sample taken is much larger than it will be possible to use for the combustion, so that it will be necessary to do something about this later on, which will be disclosed at the proper moment. However, carbon dioxide and oxygen are apt to occur in very small amounts in some gas samples, and for this reason it is obviously necessary to take as large a sample as possible for their determination by absorption.

Measurement of the sample.—The gas sample taken into the burette is now under positive pressure. Before the burette is opened to the manometer, the pressure within the burette is adjusted to approximately atmospheric.

This is done as before by opening *1* and manipulating the leveling bulb L_1 by hand until the mercury within the bulb and burette are roughly at the same level. Cock *1* is then closed, L_1 placed on R_1, and *2* and *4* opened to connect the manometer to the burette. If the pressure within the burette is greater than the compensator pressure, the mercury within the compensator arm of the manometer will rise over the platinum contact. Cock *1* is then opened until the mercury drops several mm below the contact point, after which it is closed and L_1 is placed on R_2. If, on the other hand, the pressure within the burette is lower than the compensator pressure, the mercury within the compensator arm of the manometer will fall below the contact point, in which case *1* may be closed and L_1 placed on R_2 immediately.

It will be observed that the rise and fall of mercury within the compensator arm of the manometer, which contains the zero or reference contact point, follow the rise and fall of mercury within the burette. No confusion should result, since the system responds to the natural reaction of the operator, who accordingly has no inhibitions to overcome as he may in the case of the usual manometer

[18] J. R. Branham has suggested a different technique. The atmospheric outlets of *14* and *15* are connected with a short length of rubber tubing. Air may then be displaced in one operation by mercury from L_2 which is forced through *15*, *14*, and *3*. This also eliminates the necessity of a drain tube to catch excess mercury flowing from the burette through *14*.

system which is ingeniously devised to confuse the tyro by placing the reference arm of the manometer in such a position that the direction of flow of mercury within the burette is reversed in the manometer. Furthermore, it will be remembered that the position of the manometer permits the distributor and burette pressures to be balanced simultaneously. Since the manometer is usually connected to a stopcock corresponding to *2* and the distributor to a stopcock corresponding to *3*, it is impossible to do this in an ordinary apparatus. The usual technique requires several alternate pressure adjustments. The burette must be balanced against the compensator, then the distributor opened to the burette, then the burette balanced against the compensator, and so on until a pressure equilibrium is thought to have been reached.

The burette is graduated to 0.2 ml, and the distance between etch marks is about 1.2 mm, so that it is possible to estimate volumes to 0.05 ml and sometimes more closely. The burette is read with one of the illuminating devices previously described, and in such a manner that the tip of the meniscus where the reading is taken presents the appearance of a curved black line.

Absorption of carbon dioxide.—The next step in the analysis is the absorption of carbon dioxide. Since the manometer arm adjacent to the distributor may contain some of the gas sample, the introduction of which often occurs during the process of pressure adjustment, the gas within this arm is displaced by lowering L_1, opening cock *1*, and allowing the mercury in the manometer to rise to stopcock *4*. Cock *1* is turned to the constriction for the final control, and the mercury is stopped just short of the bore of cock *4*, which is then closed to the position ⊥.

The pressure of the gas within the burette is now reduced, and must be brought back to atmospheric or slightly in excess thereof before opening stopcock *13* to admit the gas to P_2 for the absorption of carbon dioxide.

The routine of absorption is as follows: Cock *1* is closed, L_1 placed on R_4, *1* is opened until the mercury in the burette rises to the mark corresponding to the original volume measured, *5* is turned to the position ⊢, *13* is then opened first upward to drain the reagent from the capillary as before described, then downward to introduce the gas through the bubbling tip. The passage should be made in about 30 seconds. After the passage, *13* is turned upward, *1* is then opened to the constriction and L_1 placed on R_1. This affords an opportunity to check the setting of *13*, since the reagent will immediately rise in the capillary inlet of P_2 if *13* is improperly adjusted, and the fact that *1* is turned to the constriction will permit the operator time to rectify a mistake before the reagent has been drawn into the distributor. Cock *1* may be opened if *13* is correctly turned, and the gas returned to the burette until the reagent is within, say, 1 cm of the dome of the pipette. Cock *1* is then closed, L_1 replaced on R_4, *13* turned downward, and *1* again opened. Three such passages will remove carbon dioxide, and the gas is finally returned to the burette for measurement, the potassium hydroxide solution in P_2 being adjusted to the etch marks by opening *1* to the constricted bore. Cock *13* is closed, *4* is opened to the distributor and the burette, and the pressure balanced approximately.

If the wall of the burette is moist, the gas within the burette should become sufficiently saturated at the end of two minutes. The pressure is then balanced against the compensator. The volume of the gas is read and noted. The difference between the volume of the sample and this volume represents the volume of carbon dioxide absorbed. If the lower portion of the burette wall is moist and the

upper portion is dry, the gas within the burette reaches saturation very slowly, sometimes requiring 20 to 30 minutes contact. If this condition obtains, time may be saved by introducing water within the burette while the sample is stored in the absorption pipette. The measurement of a gas which is not saturated with water introduces considerable error in the analysis. Errors arising from this source are frequently made in ordinary practice, and the analyst should take especial precautions to avoid them.

Absorption of oxygen.—The gas is now displaced from the arm of the manometer connected to the distributor, the pressure in the burette again adjusted to slightly in excess of atmospheric, and the remaining gas sample passed from the burette into P_3, stopcock *6* being turned to the position ⊢. The absorption is conducted as before, except that at the end of the second passage the gas is passed from the burette into P_2. This step removes the oxygen which was retained as part of the gas left in the capillaries of P_2 between the reagent and cock *13*, and in the capillary between stopcocks *5* and *13*. The total amount of oxygen thus removed by dilution will usually be small, and this step may be omitted for a technical analysis; but for exact analysis the operation is included. The third passage should remove the oxygen unless it was present in a larger amount than 20 per cent, in which case a fourth passage is advisable. After the removal of the oxygen, the gas is returned to the burette and the remaining volume measured as before. The difference between the volume after absorption of carbon dioxide and this volume represents the volume of oxygen absorbed.

Precautions.—It will be remembered that the solutions in P_2 and P_3 remove water vapor from the gas. The presence of water on the wall of the burette should always be assured before measuring the final volume after absorption. If water has disappeared from the burette, it must be added while the gas is stored in one of the two pipettes. Furthermore, the solutions should not be used after their absorbing power has been expended. The potassium hydroxide solution presents no real difficulties, since the formation of carbonate crystals indicates the need of its replacement.

It is often desirable to check the completeness of absorption with the alkaline pyrogallol solution. This is easily done by conducting the absorption in the ordinary manner, reading the residual gas volume, and then passing the gas back into the reagent and again reading the residual volume. All guesswork is eliminated by this operation.

The combustion.—The volume of oxygen taken should be in excess of the volume required to burn the gases present. In some cases a knowledge of the source of the gas sample may roughly establish its approximate composition, in which case the oxygen requirement may be more closely approximated than in the case of a completely unknown sample. In the case of an unknown sample the oxygen for combustion should be calculated on the basis of the component requiring the largest amount. This will ordinarily represent a large excess, but subsequent check analyses may be performed without the inconvenience of handling volumes larger than may be necessary.

In the present instance the gas mixture selected for analysis contains hydrogen and carbon monoxide, each of which requires 0.5

volume of oxygen per volume; and methane, which requires 2 volumes of oxygen per volume. If the sample were pure methane the oxygen required for a 10 ml sample would be 20 ml, and the air required would be approximately five times this, or 100 ml, which is the limit of the capacity of the burette. Since the sample is not pure methane this volume of air would represent some excess of the oxygen requirement. The first analysis may then be made upon this basis, but when the composition has been determined, a second and third analysis should be made with a much larger sample taken for the combustion. The operator has only to consider that the volume of air plus sample when burned should not yield a volume of gas (after contraction upon burning) in excess of the capacity of the burette. This is, of course, merely for the sake of convenience, since the contraction after combustion and the carbon dioxide produced upon combustion might be measured in successive steps if this became necessary.

Let us now consider the composition of the gases within the apparatus. At the beginning, the distributor and the distributor arm of the manometer contained nitrogen under the compensator pressure. The burette contained the sample of gas. At the present moment, after the removal of carbon dioxide and oxygen, the distributor and manometer contain some of the original nitrogen plus some of the original gas sample less its carbon dioxide and oxygen, and the burette contains this gas plus some of the nitrogen originally present in the distributor and manometer.

The mixtures are, of course, at the fixed pressure of the compensator. Now if it were possible to use all of the gas sample for the combustion, we could proceed at once. But since we are limited to a smaller volume of sample than is actually present, we must either discard the major portion of the sample within the burette, retaining say 10 ml for the first analysis, or we must discard all of the sample and take a fresh portion from P_1 for the combustion. Either method is possible, but the first method, that is, discarding a portion of the gas contained in the burette after the absorption of carbon dioxide and oxygen, requires some additional knowledge. It is apparent that in discarding a portion of this gas we have discarded an unmeasured amount of nitrogen, and at the same time left a portion of the gas in the manometer and distributor, which has not been measured with the smaller portion retained in the burette, but some of which will react in the combustion pipette. It is evident, then, that to perform the analysis in this way, we must know the volume of the manometer arm and the volume of the portion of the distributor occupied by this mixture. If these volumes are known, we may then make the calculations which are necessary to determine exactly what volume of gas sample is retained for the combustion. In other words, since the original balanced condition of the system is upset by discarding a portion of sample, we must reestablish a new balanced condition by correcting for the nitrogen removed. The discussion of this technique will be left for the present and considered again with the description of the third analytical procedure.

Meanwhile, the procedure will be continued on the basis that the necessary correction will be made automatically by the apparatus rather than by the operator or, rather, that the apparatus maintains its original balanced condition. When this requirement is made of

the apparatus, the apparatus in turn retaliates by requiring of the operator some additional manipulation. This will now be explained.

It will be assumed in the following discussion that the operator is sufficiently familiar with each step of manipulation necessary to perform the following operations:

1. Introduce a sample.
2. Adjust the pressure within the distributor or burette or both simultaneously to equal that of the compensator.
3. Measure a gas volume.
4. Conduct an absorption.

The various manipulative steps for each of the operations will, therefore, be omitted, and only the appropriate details necessary to accomplish a new operation will be given.

The procedure which follows is designed for the use of a fresh sample of gas for the combustion.

The gas confined in the distributor arm of the compensator is transferred to the burette, leaving the mercury in the manometer just below the bore of *4*, which is turned to the position ⊥. The gas is then expelled from the burette, *2* is now turned to connect the distributor, and about 50 ml of nitrogen from P_5 is drawn into the burette, after which it is passed into P_2 and P_3 and returned to the burette. The manometer is now opened to the distributor and burette, the pressure is adjusted to that of the compensator, *2* is turned to *3*, and the gas expelled from the burette. About 30 ml of air is drawn into the burette and expelled, thus flushing out the atmospheric outlet of *3*. The air for the combustion, about 99 ml, is now drawn into the burette and measured, *4* being turned to the position ⊢ during the pressure adjustment. *5* and *6* are now turned to the position ⊥, *7* to the position ⊢, *4* to the position ⊥, and the air is transferred from the burette to P_4, mercury being taken to the bore of *2*, which is then closed. The pressure within P_4 is adjusted to approximately atmospheric by raising or lowering L_4. Cock *11* is closed and *4* turned to the position ⊢. (It may be noted that the pressure balance has been slightly altered because of the fact that the gas confined in the capillary connecting cocks *2* and *4* is at approximately atmospheric pressure at the end of the above operation, and should be confined under the fixed compensator pressure. The error introduced is negligible, however, since this volume is not over 0.1 ml and a pressure change of several millimeters of mercury would not effect a change of volume measurable on the burette. If, however, a burette capable of much more accurate measurement is used, this error may be eliminated by adjusting this pressure to that of the compensator. To do this, *4* is turned to the position ⊤ and the adjustment made by lowering L_3 until the mercury in the compensator arm of the manometer is several millimeters below the contact point. The rubber tubing connecting L_3 and P_4 is now closed with a screw clamp, L_3 is placed on R_7, and the adjustment completed by admitting mercury to P_4 at a controlled rate by slowly opening the screw clamp. Cock *11* is closed at the instant the lamp flashes on.)

Cock *2* is now turned to *3*, *3* to the atmosphere, and mercury from the burette forced through the bore of *3*, which is then turned to P_1. A fresh sample of gas is now taken into the burette. The volume of this sample, which is to be burned in P_4, must be small enough so that some oxygen remains after the combustion has taken place. (Refer to previous discussion.) Since this gas contains carbon dioxide and oxygen which will take part in subsequent reactions, a correction must be made for the known amounts of these gases when the analysis is calculated. This volume is measured, pressure adjustment being made with cock *4* remaining in the position ⊢. After the volume is measured the gas is displaced from the manometer into the burette, *2* is closed, *4* is turned to the position ⊥, and the pressure in the burette is adjusted by L_1 to very slightly in excess of atmospheric.

The current is now applied to the combustion spiral and the rheostat is adjusted until the platinum wire glows with an intensity usually described as a dull cherry red. The glass shield is swung in front of the pipette. L_1 is placed on R_4. *7* is turned to the position ⊢, *6* and *5* to the position ⊥, and L_3 is adjusted to place the gas in P_4 under approximately atmospheric pressure. The pressures in P_4 and the burette must at first be carefully regulated so that (1) no gas passes from P_4 back to B and (2) no sudden surge of gas passes from B to P_4. The flow of gas

from the burette to P_4 should be slow and even. Cock *1* is opened to the constriction and *11* is opened a few seconds later. The operator's hand is kept on the rheostat controlling the current. As the gas enters the pipette and combustion starts, the platinum wire will suddenly glow brightly. Its temperature should never exceed something short of white heat or the spiral may fuse. (If this happens, the spiral must be replaced. To do this, the gas flow is immediately stopped by closing *2*, *1*, *11*, and *7*, the gas in P_4 is transferred over mercury to a reservoir connected to *9*, and returned to P_4 after the spiral has been replaced and the train refilled with nitrogen from P_5). The temperature of the spiral is kept at this practical maximum during the combustion. It will be necessary to regulate the rheostat to accomplish this, since the spiral will gradually cool as the major portion of the gas is burned. Lower wire temperatures may be used for hydrogen and carbon monoxide than for methane. If the latter gas is not present, the lower temperatures are best, since some trace of nitrogen may be oxidized at the higher temperatures. The operator will soon be able to work out a practical scheme involving the proper rheostat range for various gases, assuming a combustion spiral of uniform length and diameter. The completeness of combustion may, of course, be checked by the method used to assure the completeness of absorption.

Ordinarily four complete passages will be sufficient to complete the combustion. This means eight passages over the wire itself, which is kept glowing at the optimum temperature at all times, as the gas passes from B to P_4 and P_4 to B. The mercury in P_4 is arrested at a level about 15 mm below the combustion spiral upon each return passage to the burette except the last, when this distance is increased to about 30 mm. As the gas cools the mercury will rise, and care must be taken at first to prevent its coming in contact with the heated dome of the pipette.

The number of passages depends on the composition of the gas, variations in temperature of the wire, and variations in rate of flow of gas over the wire. The beginner will do well to check the completeness of combustion until he is familiar with the characteristic behavior of his samples. It is important that the first passage be made slowly, in order that the gas may be reduced to a composition safely below the explosion limits of the mixture. Otherwise, a regrettable accident may occur upon the second passage, and while the operator's person has been provided with protection, his nervous system, and what is more important, the apparatus, may suffer some disintegration. The second, third, and fourth passages may be made with more speed, say 1 minute per passage, while the first should take 2 to 3 minutes.

After the fourth passage some of the gas is left in the pipette, the current is turned off, *11* is closed and L_3 adjusted to leave the gas in P_4 under slight pressure as it cools. When the dome of the pipette has cooled, the gas is transferred to the burette, adjusted to approximately atmospheric pressure, the manometer opened, and the burette and distributor adjusted to the compensator pressure. The gas volume is measured. The difference between the sum of the volumes of air and gas taken for combustion, and this volume represents the contraction on burning.

The carbon dioxide produced by combustion is now determined by absorption in P_2. The gas is first displaced from the manometer into the burette, and after two passages into P_2 the major part of the gas is returned to the burette and thence transferred to P_4 (for a technical analysis the spiral is not heated) in order to regain the carbon dioxide left with the gas contained in the train and pipette connection. This step is important, since a small error in the measurement of carbon dioxide produced by combustion is multiplied in the final calculations. The gas is again passed into P_2 and after the absorption is complete the volume of the carbon dioxide produced is measured and noted. The procedure for an exact analysis differs in that the combustion

spiral is heated during the passage of the gas after the initial absorption of carbon dioxide. At the termination of the first combustion the partial pressure of carbon dioxide is often high enough to retard the reaction, but after its removal the last traces of combustible gases are burned without delay. The amount of gases burned during this second combustion is usually very small. The additional contraction is measured before the absorption of carbon dioxide.

The oxygen consumed during the combustion is now determined by measuring the excess oxygen remaining after combustion. The gas is accordingly passed twice into P_3, then into P_4 and P_2 to regain (by dilution) the oxygen remaining in the distributor, then into P_3 to complete the absorption, after which the residual volume is measured and noted. Passages into P_4 and P_2 as noted above may sometimes be omitted for a technical analysis, but never for an exact analysis.

This completes the various operations required during the analysis.

Preparation of the apparatus for a second analysis.—Since all of the hydrogen, carbon monoxide, and methane has been burned to water and carbon dioxide, and all carbon dioxide and oxygen removed by absorption, the gas remaining within the apparatus should be nitrogen.

A is turned to admit atmospheric pressure to the compensator, and then closed for the second analysis. (We have already seen how convenient it is to have the fixed compensator pressure approximately equal to that of the atmosphere, because of rough adjustments made by L_1 and L_3.) All but approximately 10 ml of the nitrogen is expelled from B. This may be discarded to the atmosphere or stored in P_5. The distributor and manometer are now balanced against the compensator, and *2* is turned to expel the residual gas from *B* to the atmosphere.

The apparatus is now in readiness for a second analysis.

5. ANALYTICAL PROCEDURE; OXYGEN USED FOR THE COMBUSTION

When oxygen is used for the combustion, rather than air, no large volume of nitrogen remains and it is possible to use the original large sample taken for the absorption analysis. This at once greatly increases the accuracy of the combustion analysis. But here again, if the necessary corrections are to be made automatically "by the apparatus itself," the procedure becomes involved for an accurate analysis, although it is simple enough for a technical or approximate analysis. These procedures will be outlined without recourse to the detailed instruction given in the preceding section, since no new manipulative processes are involved.

The apparatus is prepared for the analysis as before. The distributor and manometer are filled with nitrogen at the compensator pressure. The sample is introduced, adjusted to the compensator pressure, and measured. The volume of this sample will be large, and may be as much as 100 ml, depending on the composition of the gas. Of course if the gas were pure CH_4, it would be possible to use only a 50 ml sample, since twice this volume of oxygen is required and the capacity of the burette is only 100 ml. Furthermore, there is a total contraction of 2 volumes per volume of CH_4 burned, so that the volume of the gas after combustion is measurable within the burette. For pure CO, 100 ml of sample might be used, the oxygen required would be only 50 ml, and the volume after combustion would be 100 ml, and so on. When the approximate composition has been determined, the analyst should compute the maximum permissible volume of sample for further analyses.

After the sample is measured, the CO_2 and O_2 are absorbed exactly as before. For a technical analysis the O_2 confined below cock *5* with the CO_2 absorption may be neglected. For an exact analysis this should be removed by dilution as before.

When the volume has been measured after the absorption of oxygen, and while the pressure is till adjusted, *4* is turned to the position ⊥. The sample in the burette is then passed into P_2 for temporary storage, mercury in the burette being taken to the bore of *2*, which is then turned to *3*. Oxygen is then taken into the burette, *4* is turned to the position ⊢, and after an initial approximate adjustment to atmospheric pressure, the burette is opened to the manometer. The volume of oxygen is then measured in the usual manner. Cock *4* is again turned to the position ⊥ and the oxygen is transferred to P_4 and *11* is closed. The gas sample is then withdrawn from P_2 to the burette, the gas contained in the manometer is also transferred to the burette, and the pressures in P_4 and the burette are adjusted as previously described for the combustion, which is forthwith conducted. The platinum wire is more apt to fuse during a combustion with oxygen, and a more careful control of the rheostat and resultant wire temperature is required.

After the combustion, the contraction is measured as before. The CO_2 produced during combustion is then determined by absorption in P_2, care being taken to remove the CO_2 confined in the distributor by passing the gas from the burette (after absorption in P_2) into P_4, thence back to the burette and again to P_2. The oxygen not used during the combustion is then determined by absorption in P_3. These steps suffice for a technical analysis.

The procedure for an exact analysis is quite another affair. After the first measurement of CO_2 produced during the combustion, the following steps are taken. The gas is first passed into P_4, and the combustible portion of the original sample that was confined below cock *5*, after the absorption analysis, is burned over the glowing platinum spiral. The further contraction from this second combustion is measured. Next the CO_2 produced by the second combustion is determined by passages into P_2, P_4, and again P_2. Then the excess oxygen is determined by absorption in P_3, with passages into P_4 and P_2 before the final passage in to P_3. Finally to complete the already long story, a measured small volume of air is added directly to the sample and the mixture (which is, of course, below its explosion limits) is again passed over the heated wire in P_4 in order to burn the combustible portion of the gas which was confined below cock *6* at the end of the absorption analysis. Following this third combustion, the contraction is measured; and then the CO_2 produced is determined by passages into P_2, P_4, and P_2, and the excess oxygen by passage into P_3, P_4, P_2, and P_3. The data are then carefully segregated, and the sums of all contractions, CO_2 volumes, and O_2 volumes are calculated. The analyst will then possibly content himself in the future with technical determinations, and that is a great pity, and prompts further aid. which, it is hoped, may be advanced in the following section.

6. ANALYTICAL PROCEDURE; WITH THE CALIBRATED MANOMETER AND DISTRIBUTOR

Many of the individual steps in the procedures already described may be eliminated if the volumes of the arm of the manometer connected to the distributor and of the several parts of the distributor itself are known. It is possible to determine these volumes by a number of simple methods, several of which will be suggested at the conclusion of this discussion. For the present we will assume that these volumes are known, and assign to them definite values. (These will be taken to approximately equal the values obtained from a calibration of one of the analytical units assembled in our laboratory.)

The largest single volume existing outside of the burette is that of the arm of the manometer which is connected to the distributor. This volume is not an absolutely fixed one, since one of its boundaries is determined by a mercury meniscus which is always adjusted to the same height in the opposite manometer arm, but may vary slightly in height within the distributor arm of the manometer because of a change in the total volume of mercury confined in the manometer with changes of temperature. Such temperature changes are never sufficiently large to affect the pressure balance during the course of a single analysis. A calculation will also show that a change of 10° C. will not change the volume of gas confined above the mercury within the distributor arm of the manometer by more than 0.01 ml. This volume may, therefore, be accepted as constant as far as the analysis goes. The remaining volumes within the distributor are bounded by the glass walls of the capillaries, with the exception of the gas confined between the reagents of the pipettes P_2 and P_3, and stopcocks *13* and *12*. Since these reagents are always adjusted to etch marks on capillary stems, the resulting variations in volume are negligible.

These volumes may now be noted.

	ml [1]
D_1, the manometer arm adjacent to the distributor	2.0
D_2, the capillary space within the distributor from cock *2* through cocks *4*, *5*, *6*, *13*, and *12* to the etch marks on the capillaries below *13* and *12*	.8
D_3, the capillary spaces within the distributor between cock *5* and the etch marks on the capillaries below *13*, and between cock *6* and the etch marks on the capillaries below *12*	.4
D_4, the capillary space within the distributor from cock *2* through *4* and *5* to 6 (that is, the horizontal portion of the distributor)	.4

Let us now review the analytical procedures already given and determine how these may be simplified, having at our command the additional information just given.

Modified procedure using air for the combustion.—The technique first described required the use of a fresh portion of sample for the combustion, and this, in turn, made it necessary to replace the gas confined within the apparatus, after the absorption analysis, with nitrogen. These manipulations require some time and trouble which may be saved.

After the absorption analysis, gas is expelled from the burette until only a small portion remains. The volume of this gas retained for the combustion is measured. Let us suppose this volume is 10 ml (which would have been required for the first analysis), while the

[1] Ordinarily this will be only 1 ml.

volume of the original sample taken for the absorptions was 100 ml, and after absorption of carbon dioxide and oxygen was 90 ml. The gas within the apparatus has been thoroughly mixed during the absorptions, so that we have within the distributor and manometer some of the nitrogen they originally contained plus some of the gas sample from the burette, and conversely, within the burette we have some of the gas sample it originally contained plus some of the nitrogen from the distributor and manometer. With the discarded portion of gas we have also discarded some of the nitrogen originally present in the distributor and manometer.

The conditions just before the absorption analysis were:

In B, 100 ml sample.

In D_1+D_2, 2.8 ml nitrogen.

The conditions after the absorption analysis and just before expelling 80 ml of the mixture from the burette were:

$$\text{In } B\left(\frac{90}{92.8}90\right)\text{ml sample}+\left(\frac{2.8}{92.8}90\right)\text{ ml } N_2.$$

$$\text{In } D_1+D_2\left(\frac{90}{92.8}2.8\right)\text{ ml sample}+\left(\frac{2.8}{92.8}2.8\right)\text{ ml } N_2.$$

The conditions after expelling 80 ml of mixture from the burette are:

$$\text{In } B\left(\frac{90}{92.8}10\right)\text{ ml sample}+\left(\frac{2.8}{92.8}10\right)\text{ ml } N_2.$$

In D_1+D_2 unchanged from the second condition.

$$\text{In } D_4\left(\frac{90}{92.8}0.4\right)\text{ ml sample}+\left(\frac{2.8}{92.8}0.4\right)\text{ ml } N_2.$$

Now it would be of advantage to eliminate the necessity of burning the combustible portion of the gas confined below 5 and 6 after the absorption analysis, since, as we have seen during the discussion in section 5, this involves additional tedious steps. We shall, therefore, arrange the procedure so that these gases remain inert and may be considered as so much nitrogen. Furthermore, the gas confined in the manometer may be treated in the same manner. We should then be interested only in the calculations:

$$\text{In } B\left(\frac{90}{92.8}10\right)\text{ ml sample.}$$

$$\text{In } D_4\left(\frac{90}{92.8}0.4\right)\text{ ml sample.}$$

The sum of these gives the volume of the original sample (less the CO_2 and O_2) which is taken for, and will react during, the combustion. This volume is $9.57+0.388$, or to reduce within the practical limits of accuracy, $9.57+0.39=9.96$ ml. Just how the percentages of the combustible components may be calculated will be developed shortly.

After the measurement of this sample, *2* is closed, *4*, *5*, and *6* are turned to the position ⊥, and the combustion is then conducted with the manometer shut off. The contraction is measured as before, then

the CO_2 produced and oxygen excess are determined. This greatly simplifies the manipulative procedure, and does not greatly add to the burden of the calculations.

To prepare the apparatus for a second analysis it is necessary to replace the confined gas with N_2, since the mixture within the apparatus now contains some proportion of combustible components which have not reacted.

Procedure when oxygen is used for the combustion.—The complication which was involved in this procedure (as described in sec. 5) was the necessity of burning the small portions of gas confined under cocks *5* and *6* at the termination of the absorption analysis. This may now be avoided by subtracting the amount of the original sample confined in these spaces from the total volume of the original sample. If 50 ml of sample was taken, the amount of sample confined in D_3 is $\left(\frac{50}{52.8}\ 0.4\right)$ ml $=0.38$ ml. The amount of sample burned would then be $50.0-0.38=49.62$ ml. The gas confined in the manometer is displaced into the burette before the combustion. The combustion is then followed by measurement of contraction, CO_2 produced, and excess oxygen, with no complications such as were experienced before. Much time is also saved.

7. DETERMINATION OF THE STEPS NECESSARY FOR AN ACCURATE ANALYSIS

The knowledge of the capacities of the manometer arm connected to the distributor and of the various parts of the distributor itself will be of further benefit. The analyst is now in the position to determine just what steps are necessary for an exact analysis. Let us suppose, for example, that 2 ml of oxygen is absorbed from 100 ml of original sample during the first passages from B to P_3. Shall the analyst pass the gas back into P_2 to effect the removal of the oxygen confined below cock *5* after the absorption of carbon dioxide? The volume of oxygen which would then be removed by this step, and which might then be absorbed, would be

$$\left(\frac{2}{100}\ 0.2\right) \text{ml} = 0.004 \text{ ml}$$

This amount could not be measured in the burette, and the extra step may be omitted. Had 20 ml of oxygen been absorbed during the first passages into P_3, the volume of oxygen confined under cock *5* would be measurable (0.04 ml) and the gas should be removed by dilution for absorption in P_3.

In a similar manner one may calculate whether or not it is necessary to perform other such steps designed to remove gases confined in the distributor by dilution with gas from the burette. It will usually be necessary to remove CO_2 confined in the distributor after the combustion. It will be remembered that a small error in the measurement of total carbon dioxide produced upon combustion will result in a larger error in the calculated composition of the mixture. This will become apparent after reading section 9, where the equations for calculating the volumes of H_2, CO, and CH_4 are given.

It may be of advantage to tabulate values, or plot them on curves, showing the volumes retained in the various capillary dead spaces as functions of the amounts of each constituent present at any step of the analysis. Data so prepared could be used as a ready reference in determining the number of dilutions necessary. The analyst will probably learn in time to reach these conclusions by mental arithmetic.

8. CALIBRATION OF THE DISTRIBUTOR AND MANOMETER

The usefulness of the work discussed in the two preceding sections depends a great deal upon the ease with which the distributor and manometer can be calibrated. It is obvious that the accidental breaking of any part will involve recalibration of the piece used for replacement, and for this reason it should be possible to make the calibration simply and quickly. As a matter of fact, there should be little danger of breakage, and if this does occur it is apt to be an absorption pipette which must be replaced. Fortunately, neither the calibration of the pipette nor of the distributor and manometer, presents any real difficulty.

Calibration of pipettes.—The empty pipette is inverted and the capillary portion connecting to the distributor is immersed in mercury. Reduced pressure is applied to the atmospheric outlet of the pipette reservoir, where the reagent is ordinarily introduced. The stopcock is slowly opened and mercury is drawn into the pipette until it passes about a centimeter beyond the etch marks. The reduced pressure within the pipette is now released, and the mercury is allowed to flow back very slowly through the partially opened stopcock. When the mercury meniscus reaches the etch mark the cock is closed and the capillary tip is removed from the mercury in which it has been immersed. The mercury which is now confined in the capillaries of the pipette is allowed to drain out into a small weighing flask. The weight of the mercury is taken and this is converted to the desired volume, by multiplying by 0.0738. (Corrections for changes of temperature, etc., are unnecessary for the small volumes of the capillary spaces.)

Calibration of the distributor.—The distributor can be calibrated by the same method. The whole piece is inverted and mercury is introduced from a reservoir temporarily connected by rubber tubing to cock *9*. The distributor is then tilted slightly and the mercury is caught and weighed as it is allowed to escape. The exit flow is controlled by opening the various cocks, and it is thus possible to calibrate each section of the distributor.

There are many alternative methods. One simple method is to mount the distributor vertically and admit water to the various sections from a 10 ml calibrated volumetric burette connected temporarily to cock *9*.

Calibration of the manometer arm connected to the distributor.—This can best be done after the apparatus is assembled and ready for an analysis.

Air is taken into the burette, the pressure is balanced against the compensator by the manometer, and the volume within the burette is read. The manometer is now connected to the combustion pipette by turning cock *4* to the position ⊣. L_3 is placed on R_6, and a screw clamp which has closed the rubber tubing connecting L_3 and P_4 is now very slowly opened until the mercury flows upward in the distributor arm of the manometer. When the mercury thread reaches the bore of *4*, this cock is turned clockwise to position ⊢ and the pressure of the gas within the burette is again balanced with the compensator, and the volume measured. The difference between the first and second volumes is the volume of the manometer arm which was sought. The measurement should be repeated several times and an average value taken.

9. CALCULATION OF THE ANALYSIS

We have now obtained the following data:

V_1 = Volume of the sample of gas.
V_2 = V_1 minus the CO_2 absorbed.

V_3 = V_2 minus the O_2 absorbed.
V_4 = Volume of oxygen taken for combustion. (If air, multiply by 0.2095.)
V_5 = Volume of gas sample taken for combustion.
V_6 = (V_4 + V_5) minus the total contraction (TC) after combustion.
V_7 = V_6 minus the CO_2 produced upon combustion.
V_8 = V_7 minus the oxygen left after the combustion, from which the oxygen consumed may be computed.

From these we obtain the volumes

Carbon dioxide = $V_1 - V_2$.
Oxygen = $V_2 - V_3$.
Total contraction = $(V_4 + V_5) - V_6$.
CO_2 produced = $V_6 - V_7$.
O_2 consumed = $V_4 - (V_7 - V_8)$.

The volumes of H_2, CO, and CH_4 are computed from equations derived from the reaction equations:

$$2H_2 + O'_2 = 2H_2O \ (TC' = 3) \quad (1)$$
$$2CO + O''_2 = 2CO''_2 \ (TC'' = 1) \quad (2)$$
$$CH_4 + 2O'''_2 = 2H_2O + CO'''_2 \ (TC''' = 2) \quad (3)$$

From these equations taken in order it is seen that:

$$H_2 = 2/3 \ TC' = 2O'_2 \quad (4)$$
$$CO = 2TC'' = 2O''_2 = CO''_2 \quad (5)$$
$$CH_4 = 1/2 \ TC''' = 1/2 \ O'''_2 = CO'''_2 \quad (6)$$

Expressing the reaction of the mixture in terms of TC, O_2, and CO_2; where TC now equals the total contraction after combustion of the mixture, O_2 equals the oxygen consumed and CO_2 equals the carbon dioxide produced during the combustion of the mixture:

$$1.5H_2 + 0.5CO + 2CH_4 = TC \quad (7)$$
$$0.5H_2 + 0.5CO + 2CH_4 = O_2 \quad (8)$$
$$CO + CH_4 = CO_2 \quad (9)$$

Solving (7) and (8) for H_2:

$$H_2 = TC - O_2 \quad (10)$$

Solving (8) and (9) for CH_4 (substituting $H_2 = TC - O_2$):

$$CH_4 = O_2 - 1/3 \ (CO_2 + TC) \quad (11)$$

Solving (8) and (9) for CO:

$$CO = 1/3 \ (4CO_2 + TC - 3O_2) \quad (12)$$

Equations (10), (11), and (12) are used to compute, from the observed data, the volumes of H_2, CO, and CH_4, in the portion of the sample taken for combustion.

If only CH_4 and H_2 are present, the equations for their volumes are:

$$CH_4 = CO_2 \quad (13)$$
$$H_2 = 2/3\ (TC - 2CO_2) \quad (14)$$

If only CO and H_2 are present, the equations for their volumes are:

$$CO = CO_2 \quad (15)$$
$$H_2 = 1/3\ (2TC - CO_2) \quad (16)$$

In either of the above cases, it is not necessary to determine the oxygen consumed. However, if this is done, a further check is afforded, since the calculations may be made upon the basis of TC and O_2 as well.

If methane and ethane are the only two combustible gases present, their volumes are computed from the equations:

$$CH_4 = 1/3\ (4TC - 5CO_2) \quad (17)$$
$$C_2H_6 = 1/3\ (4CO_2 - 2TC) \quad (18)$$

These calculations may also be checked by computing from TC and O_2 and from CO_2 and O_2. It will be noted, however, that if more than two hydrocarbons are present it is not possible to determine the composition of the mixture by a combustion. In such cases, the mixture may be separated by fractional distillation.[20]

The percentage of nitrogen may be calculated (for a technical analysis) as equal to 100 minus the sum of the percentages of the other components. The actual volumes of nitrogen can be directly measured for an exact analysis. If all of the gas has been passed over the combustion spiral during the analysis, nitrogen alone remains at the end of the analysis, and this is directly measured. If any of the original sample has been confined below cocks *5* and *6* or in the manometer arm, the volume of this portion of the sample which has not reacted during the combustion is calculated and corrected for.

The calculation of the actual percentages of the components is illustrated in the following example.

It will be well to go through an actual calculation, and after this to assume small errors in the gas volumes for each step of the analysis and observe the significance of these errors. For this purpose we shall assume that the analysis has given the following observed gas volumes:

	ml
Sample	99. 10
After absorption of CO_2	95. 15
After absorption of O_2	94. 65
Oxygen taken for combustion	98. 35
After combustion	81. 75
After absorption of CO_2 produced by combustion	34. 40
After absorption of O_2 left after combustion	8. 45

[20] This method is described by Martin Shepherd in B. S. Jour. Research 2 (R. P. 75), p. 1145; 1929; The Separation of Natural Gases by Isothermal Fractional Distillation.

From these data we can compute:

Volume of CO_2 in sample $= 99.10 - 95.15 = 3.95$ ml.
Volume of O_2 in sample $= 95.15 - 94.65 = 0.50$.
Total contraction $= 94.65 + 98.35 - 81.75 = 111.25$.
Volume of CO_2 produced $= 81.75 - 34.40 = 47.35$.
Volume of excess $O_2 = 34.40 - 8.45 = 25.95$.
Volume of O_2 used $= 98.35 - 25.95 = 72.40$.
Volume of H_2 burned $= 111.25 - 72.40 = 38.85$.
Volume of CO burned $= 1/3\ [4(47.35) + 111.25 - 3(72.40)] = 27.82$.
Volume of CH_4 burned $= 72.40 - 1/3\ [47.35 + 111.25] = 19.53$

The percentages of CO_2 and O_2 are directly obtained:

$$\text{Per cent } CO_2 = \frac{3.95 \times 100}{99.10} = 3.99$$

$$\text{Per cent } O_2 = \frac{0.50 \times 100}{99.10} = 0.51$$

To obtain the percentages of H_2, CO, and CH_4, a correction must be made for the volumes of these gases which were confined below stopcocks *5* and *6* after the absorption analysis and which, therefore, were not burned during the combustion. The volume of this space was given as 0.4 ml. At the beginning of the analysis the apparatus contained 2.8 ml N_2. After absorption of CO_2 and O_2 there remained 94.65 ml of gas in the burette. The fraction of the 2.8 ml N_2 which is confined within the 0.4 ml space after the absorption analysis is, therefore,

$$0.4 \frac{2.8}{2.8 + 94.65} = 0.01 \text{ ml}$$

The 0.4 ml space, therefore, contains $0.4 - 0.01 = 0.39$ ml of the original sample (less its CO_2 and O_2) which was not burned. The volume of the original sample minus the CO_2 and O_2 was 94.65 ml. Of this, $94.65 - 0.39 = 94.26$ ml was burned. The volumes of H_2, CO, and CH_4 found were, therefore, the result of burning 94.26 ml of the original sample. Since 94.65 ml of the sample should have been burned, it is obvious that the observed volumes of H_2, CO, and CH_4 are too low. These may be corrected to the basis of the original sample of 99.10 by multiplying each volume by the factor $\frac{94.65}{94.26}$, or the original sample may be corrected to the basis of the observed volumes of H_2, CO, and CH_4. The latter method is simpler. The fraction x of the sample which should be used to compute the percentages of H_2, CO, and CH_4 from their observed volumes is obtained:

$$\frac{94.65}{94.26} = \frac{99.10}{x} \text{ or } x = 98.69$$

The percentage of H_2, CO, and CH_4 are now computed:

$$\text{Per cent } H_2 = \frac{38.85 \times 100}{98.69} = 39.37$$

$$\text{Per cent CO} = \frac{27.82 \times 100}{98.69} = 28.19$$

$$\text{Per cent } O_2 = \frac{19.53 \times 100}{98.69} = 19.79$$

The percentage of N_2 in the original sample can also be computed. The volume of the original sample confined within the 0.4 ml space was 0.39 ml. Of this volume there were

$$\frac{38.85 + 27.82 + 19.53}{94.26} 0.39 \text{ ml} = 0.36 \text{ ml of } H_2, \text{ CO and } CH_4$$

which were not burned. This 0.36 ml of unburned gas remains at the end of the analysis and is measured with the residual volume of nitrogen. The amount of nitrogen contained in the original sample is therefore the observed residual volume minus the volume of unburned gas, or $8.45 - 0.36 = 8.09$ ml. The percentage of N_2 is then calculated:

$$\text{Per cent } N_2 = \frac{8.09 \times 100}{99.10} = 8.16$$

The sum of the percentages of the constituents is now taken:

CO_2	3.99
O_2	.51
H_2	39.37
CO	28.19
CH_4	19.79
N_2	8.16
Total	100.01

The analyst should determine the significance of errors made in the various steps of the analysis. This can be done by assigning arbitrary errors to the observed volumes and recalculating the results. For example, suppose errors of 0.05 ml had been made in the measurements of the volume after combustion and the volume after absorption of the CO_2 produced by combustion, and that these errors occurred in opposite directions. The burette readings are then

	ml
S	99.10
$-CO_2$	95.15
$-O_2$	94.65
$+O_2$	98.35
$-TC$	81.70
$-CO_2$	34.45
$-O_2$	8.45

The computed results are:

	ml
CO_2	3.99
O_2	0.51
H_2	39.47
CO	28.12
CH_4	19.76
N_2	8.16
Total	100.01

Differences of 0.1 per cent H_2, 0.07 per cent CO, and 0.03 per cent CH_4 were obtained. If the combustion is expected to check within 0.1 per cent it is apparent that the errors in measuring the volumes, which determine the total contraction, CO_2 produced, and oxygen consumed, must be small. For example, suppose the CO_2 produced upon combustion had been determined by passage into P_2 alone, rather than by passages into P_2, P_4, and P_2. The CO_2 left in the train and not determined would have been approximately $\frac{47.35}{81.75}\ 0.3 = 0.17$ ml, and this error would have resulted in much larger errors in the calculated results than were obtained in the example given above. Similarly, the oxygen left below cock *5* and in the distributor after the absorption of the CO_2 produced on combustion is $\frac{25.95}{47.35}\ 0.4 = 0.22$ ml, and this must be regained by dilution and determined by absorption.

Calculations of this sort will enable the analyst to avoid unnecessary steps on the one hand and deplorable errors on the other.

V. SUMMARY

The gas analysis apparatus which has been described possesses a number of new and desirable features and retains the better features of older apparatus. Among them are:

1. A burette which eliminates parallax.
2. A device which provides good illumination for reading the burette with precision.
3. A combined manometer-compensator which is compact and much less fragile than the usual type. The manometer eliminates the significant capillary errors which occur with the variety in common use. The pressure balance is obtained by electric contact, which results in much greater accuracy than is possible with the usual methods, and greater speed.
4. A special control stopcock, which insures not only accuracy in balancing the manometer, but practically eliminates the danger of drawing reagents from the pipettes into the distributor.
5. A water jacket which eliminates the objectionable large rubber stopper ordinarily used.
6. A distributor or manifold which eliminates much of capillary dead space, and is calibrated to permit the use of a special method for exact analysis which makes it possible to obtain accuracy without the usual large number of operations.
7. An absorption pipette in which reaction is very rapid.
8. A combustion pipette which eliminates the many undesirable features of the common type.
9. A sampling pipette which is designed to permit the convenient manipulation of gas samples without possibility of contamination.
10. Means for practically eliminating the leakage which commonly occurs in the ordinary commercial apparatus.
11. An arrangement of assembly which permits unusual conveniences in manipulation. The burette and distributor may be balanced simultaneously against the compensator. The usual error arising from diffusion into the manometer is eliminated. The distributor may be flushed with nitrogen from either end.

12. An apparatus support constructed entirely of metal which is free from warping or swelling and is designed to make easy the assembly and replacement of all parts of the apparatus.

Several procedures for making technical and exact analyses are given. These procedures depend upon (1) computing the necessary corrections from the observed data and the known calibration of the distributor, and (2) automatically eliminating these corrections by additional operations within the apparatus itself. Since the former method eliminates many of the operations which are required in the latter, it should prove of decided advantage where accuracy is required and a minimum of time is available, and is perhaps the most hopeful advance to be offered in the operating technique of this kind of gas analysis.

The combination of the improved apparatus and method proceeds along the desirable line of development whose aim is a greater accuracy obtained in a shorter time.

WASHINGTON, November 14, 1930.

DETERMINATION OF SMALL QUANTITIES OF VOLATILE ORGANIC ACIDS IN SULPHURIC-ACID SOLUTIONS

By D. N. Craig

ABSTRACT

A procedure is described for separating small quantities of volatile organic acids from the electrolyte of lead storage cells and from wood separator extracts containing 30 to 40 per cent of sulphuric acid. A subsequent procedure for separating acetic from formic acid in the distillates is also described. A modified differential potentiometric method for titrating acid solutions of the order of a few thousandths normal was found to be reliable in estimating the acidities of the distillates. Some phenolphthalein titrations of the distillates are compared with electrometric titrations.

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I. INTRODUCTION

In a study of the corrosive effect of various organic substances on the plates of lead storage cells, it was found that under certain conditions small quantities of acetic acid in the electrolyte definitely corroded the positive plates. In this connection, as well as in a study of the adequacy of treatment of wood separators, the necessity arose for determining the percentage of acetic acid in solutions containing 30 to 40 per cent of sulphuric acid.

For most purposes the volatile organic acid content of the electrolyte in a cell, which has been cycled, may be considered to be acetic. It is, however, to be expected that a considerable percentage of the volatile acids formed by partial hydrolysis of wood separators in sulphuric-acid solutions is formic acid. Because of the pronounced corrosive effect of acetic acid on the positive plates, it was desirable to distinguish between the percentage of acetic acid and the other volatile organic acids in the sulphuric-acid extracts of the separators.

Schorger [1] has studied the hydrolysis of wood by sulphuric acid and his procedure for distilling the volatile acids from a 1.5 per cent sulphuric-acid solution is given by Hawley and Wise. The percentage of acetic acid in a newly assembled cell may, however, be as small as a few hundredths of 1 per cent and dilution of the electrolyte to 1.5 per cent of sulphuric acid previous to distilling would in turn reduce the concentration of acetic acid to a very low value. Since the volatile organic acid content of sulphuric-acid solutions of separator extracts decreases with the adequacy with which the separator has been treated, it is likewise desirable to avoid dilution before distilling the volatile acids.

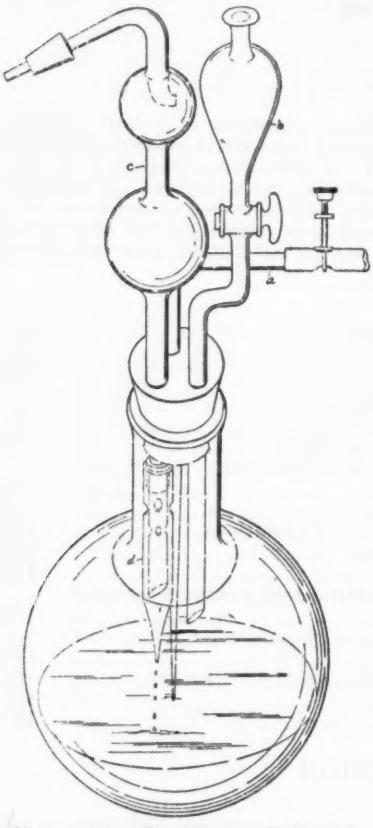

FIGURE 1.—*Distillation flask with fittings*

The object of this investigation was to establish a suitable procedure for determining small amounts of volatile organic acids in battery electrolytes, or in sulphuric-acid solutions of extracts of treated separators. This was accomplished by converting the sulphuric acid in part into sodium sulphate, and the remainder into the acid sulphate, with concentrated sodium hydroxide and distilling to dryness, thereby avoiding unnecessary dilution of the volatile acids. A known portion of the distillate, containing the volatile acids, was then titrated for total acidity. Another portion of the distillate was then treated with potassium permanganate and sodium carbonate to remove reducing organic acids, and, after again distilling, the second distillate was titrated for acetic acid.

The titrations were made with barium hydroxide solutions, using a differential potentiometric method. For the purpose of comparison, some titrations were made with phenolphthalein.

II. DISTILLATION OF VOLATILE ORGANIC ACIDS

Fifty-milliliter samples of sulphuric-acid solution (1.250 specific gravity) containing known quantities of acetic and formic acids, were used in the distillations for the purpose of checking the method. A solution of approximately 20 per cent sodium hydroxide, equivalent to the sulphuric acid in 35 ml of the sample, was added to the

[1] Hawley and Wise, The Chemistry of Wood, p. 132; 1926.

sample in a wide-mouthed, round-bottomed, 1,000 ml flask, containing a few pieces of porous plate. The flask was then provided with a rubber stopper containing: A glass tube, *a*, drawn out to a capillary, closed with a rubber tube and pinchcock, and extending to the bottom of the flask; a dropping funnel, *b;* a distilling column, *c*; and a tube, *d*, covering the lower end of the column. The flask, with its fittings, is shown diagrammatically in Figure 1.

The tube, *d*, the lower end of which is drawn to a capillary, is attached to the column by a rubber washer, fitting against the large rubber stopper. The staggered arrangement of the holes in the tube and in the distilling column aids in preventing mechanical carrying of spray into the condenser. A portion of the condensate collects in the capillary end of tube, *d*, and prevents vapor or spray from entering directly into the distilling column. A supply of ice water served to cool the 22-inch condenser, as well as a receiving flask, which was connected to an aspirator and a manometer. The rate of distillation was controlled by regulating the aspirator and adjusting the pinchcock. The temperature of a water bath surrounding the flask was maintained at 65° to 75° C., except at the end of the distillation, when it was raised to 80° to 85° C. After distilling to dryness, the temperature was lowered to about 70° C. and a few milliliters of water was added to the distilling flask by means of the separatory funnel, after which the temperature was again raised to about 85° C. and the distillation again carried to dryness. This procedure was followed twice at the end of each distillation so that the last traces of organic acids would be carried over. The distillate was transferred to and diluted in a volumetric flask and a known volume titrated for total acidity.

III. ELIMINATION OF FORMIC ACID IN THE DISTILLATES

Following the procedure of Jones [2] for oxidizing formic acid with potassium permanganate, 50 or 100 ml portions of the distillates containing both formic and acetic acid were added, in the distilling flask to 15 ml of molar sodium carbonate solution and an excess of approximately 0.1 *N* potassium-permanganate solution. The distilling apparatus was again assembled and the solution heated under atmospheric pressure for approximately 20 minutes at 80° to 90° C. Ten milliliters of sulphuric acid (1.250 specific gravity) together with a solution of sodium sulphate equivalent to 20 ml of sulphuric acid (1.250 specific gravity), was then added through the dropping funnel to the solution in the flask. The solution was then distilled, as described above, and a known portion of the distillate titrated for acetic acid. From the acidities of the first and second distillates and the dilution factors the percentage of each acid in the original sample can be calculated.

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[2] Am. Chem. J., 17, p. 539; 1895.

IV. DIFFERENTIAL TITRATION OF DILUTE ACID SOLUTIONS

The acidities of the distillates were determined with modifications of differential potentiometric methods described by Clarke and Wooten [3] and MacInnes and Dole.[4] A diagrammatic sketch of the cell vessel used in the present experiments and differing in some respects from that used by the above authors is shown in Figure 2.

The vessel was provided with a rubber stopper, through which projected a bubbling tube, *a*; a 25 ml burette, *b*; a shielding tube, *c*, containing the retarded electrode, *d*; and the electrode, *e*, projecting through the glass tube, *f*. The electrodes consisted of bright platinum wires sealed into glass tubes, containing a few drops of mercury for making contact with the leads to the potentiometer. The electrode tubes were held in place by means of small corks which were sealed into the flared openings of the tubes, *c* and *f*, with paraffin. The lower end of the shielding tube was drawn to such size as to retard diffusion, yet sufficiently large to give satisfactory galvanometer sensitivity. To the upper end of the shielding tube was attached a side arm for introducing hydrogen. Through a 3-way stopcock, *g*, hydrogen could be passed through the tube, *a*, or through the shielding tube, *c*, thereby making it possible to stir the main portion of the solution, while titrating, or to flush out the shielding tube when desired. A side tube attached to the upper end of the tube, *f*, provided a means of escape for the hydrogen. The hydrogen was passed through a heated quartz tube containing palladiumized asbestos and in turn through a tower of soda lime. By momentarily opening the stopcock, *h*, after flushing out the shielding tube, sufficient solution rises in the shielding tube to cover the retarded electrode. A suitable potentiometer with a lamp and scale galvanometer served for measuring the potential differences. The barium hydroxide solutions used in the titrations were protected from carbon dioxide and were made by diluting saturated barium hydroxide solutions to approximately the strength desired with carbon dioxide free distilled water.

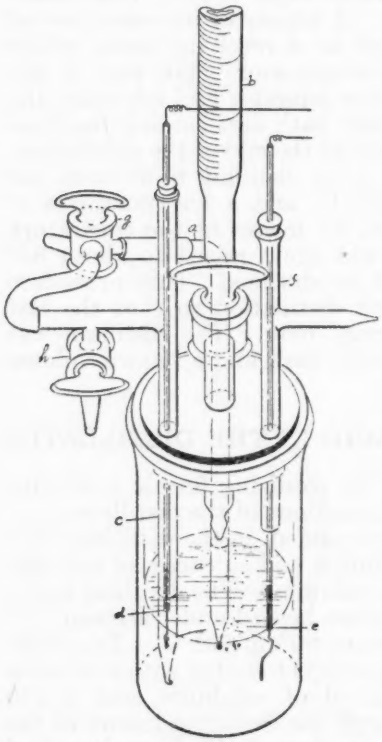

FIGURE 2.—*Cell vessel for differential potentiometric titrations*

The solution to be titrated was introduced into the vessel, together with a known quantity of potassium-chloride solution and a little

[3] J. Phys. Chem., **33**, p. 1468; 1929.

[4] J. Am. Chem. Soc., **51**, p. 1119; 1929.

quinhydrone. The vessel was then fitted with the rubber stopper and arranged as shown in the sketch. Hydrogen was then allowed to bubble through the solution with frequent flushing of the shielding tube, until satisfactory equilibrium was obtained as indicated by the constancy of the potential differences. The departure of the initial potential difference from zero seemed to increase somewhat with the rate at which hydrogen passed through the solution and the proximity of the hydrogen bubbles to the electrode. The sign of the potential difference indicates a slight catalytic reduction of the quinhydrone in the presence of hydrogen and platinum. No difficulty was experienced, however, in obtaining constant readings and, although the potential difference at the start of a titration was often as much as 15 mv, the increase in potential for additions of the same quantity of base was uniform for titrations involving the same acid and base solutions. When the titration was approximately 1 ml from the end point, as indicated by the potential changes, the shielding tube was again flushed and a new "zero" reading was noted. Potential readings were then noted for smaller increments of base. In this respect the method of titrating differed from that of the above authors [5] whose arrangement made no provision for stirring the main portion of the solution without flushing the shielding tube, making it necessary to obtain a new zero reading after each addition of base or to depend upon diffusion to establish equilibrium. The arrangement used in the present experiments permits continuous stirring and titrating of the main portion of the solution without necessitating a new zero reading until close to the end point.

V. TITRATION OF DILUTE SOLUTIONS OF KNOWN ACIDITIES

1. PREPARATION OF DILUTE SOLUTIONS OF HYDROCHLORIC, ACETIC, AND FORMIC ACIDS

Before distilling any of the samples, it was desirable to know the precision with which the results of the electrometric titrations could be used in judging the success with which the distillations had been carried out. For this purpose solutions of known acidities, of the order of a few thousandths normal, were titrated. These solutions were prepared by diluting more concentrated solutions of hydrochloric, acetic, and formic acids, the normalities of which were found to be: Hydrochloric, 0.5117; acetic, 0.2979; and a second solution, 0.4957; and formic, 0.2047. The solution of hydrochloric acid was standardized by the silver-chloride method and against potassium acid phthalate. A portion of the hydrochloric acid solution, diluted to approximately 0.1 N, was then titrated with a solution of barium hydroxide, which in turn was used to titrate solutions of acetic and formic acids made by diluting portions of the original acids to approximately 0.1 N. Phenolphthalein was used as the indicator in these titrations.

2. ESTIMATION OF END POINT

In Table 1 detail data are given for the titration of dilute solutions of hydrochloric, acetic, and formic acids, and also a portion of a distillate containing acetic and formic acids. ΔE denotes the change in

[5] See footnotes 3 and 4, p. 172.

potential between the electrodes when an increment of base ΔB is added to the solution. For the purpose of graphical interpolation the values of $B+\frac{\Delta B}{2}$ are given for the four curves in Figure 3. The agreement of the end points determined directly by noting the volume

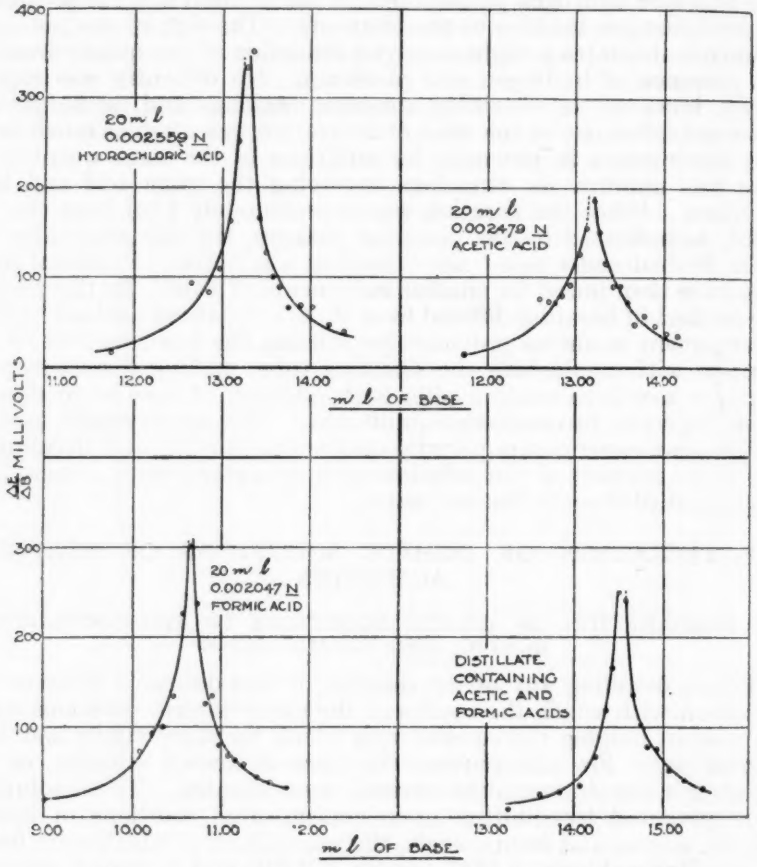

FIGURE 3.—*Differential potentiometric titration curves*

of base corresponding to a maximum value of $\frac{\Delta E}{\Delta B}$ and by graphical interpolation, indicates that for most purposes the shorter method is as satisfactory as the graphical method. In these titrations, the volume of the solution in the shielding tube was always less than 0.5 ml and the tube was flushed when the titration was within 1 ml of the end point on the acid side.

TABLE 1.—*Experimental results for titration of dilute solutions*

20 ml 0.002559 *N* hydrochloric acid

Burette readings	ΔB	$B+\frac{\Delta B}{2}$	ΔE	$\frac{\Delta E}{\Delta B}$
ml	*ml*	*ml*	*mv*	
[1] 0.10				
3.00	2.90	1.45	17	6
6.00	3.00	4.50	15	5
9.00	3.00	7.50	21	7
11.00	2.00	10.00	19	10
	1.54	11.77	26	17
	New "zero" observed			
12.54				
12.80	.26	12.67	24	92
12.92	.12	12.86	10	83
13.05	.13	12.99	14	108
13.13	.08	13.09	13	162
13.21	.08	13.17	20	250
13.30	.09	13.26	30	333
13.38	.08	13.34	28	350
13.47	.09	13.43	15	167
13.54	.07	13.51	9	128
13.62	.08	13.58	8	100
13.71	.09	13.67	8	89
13.83	.12	13.77	8	67
13.96	.13	13.90	9	69
14.11	.15	14.04	10	67
14.30	.19	14.21	9	47
14.50	.20	14.40	8	40

20 ml 0.002479 *N* acetic acid

Burette readings	ΔB	$B+\frac{\Delta B}{2}$	ΔE	$\frac{\Delta E}{\Delta B}$
ml	*ml*	*ml*	*mv*	
[1] 0.35				
3.00	2.65	1.33	30	11
6.00	3.00	4.50	23	8
9.00	3.00	7.50	22	7
11.00	2.00	10.00	15	8
	1.53	11.77	18	12
	New "zero" observed			
12.53				
12.68	.15	12.61	11	73
12.75	.07	12.72	5	71
12.82	.07	12.79	5	71
12.91	.09	12.87	7	78
13.00	.09	12.96	8	89
13.08	.08	13.04	10	125
13.17	.09	13.13	14	155
13.24	.07	13.21	13	186
13.32	.08	13.28	12	150
13.40	.08	13.36	9	112
13.48	.08	13.44	7	88
13.56	.08	13.57	7	88
13.63	.07	13.60	5	71
13.72	.09	13.68	4	45
13.85	.13	13.79	7	54
13.97	.12	13.91	5	42
14.09	.12	14.03	4	33
14.25	.16	14.17	5	31

20 ml 0.002047 *N* formic acid

Burette readings	ΔB	$B+\frac{\Delta B}{2}$	ΔE	$\frac{\Delta E}{\Delta B}$
ml	*ml*	*ml*	*mv*	
[1] 0.19				
4.00	3.81	1.91	29	8
8.00	4.00	6.00	36	9
10.00	2.00	9.00	36	18
	.17	10.09	12	71
	New "zero" observed			
10.17				
10.28	.11	10.23	10	91
10.41	.13	10.35	13	100
10.53	.12	10.47	16	133
10.61	.08	10.57	18	225
10.70	.09	10.66	27	300
10.78	.08	10.74	19	237
10.87	.09	10.83	11	122
10.93	.06	10.90	8	133
11.02	.09	10.98	7	78
11.11	.09	11.07	6	67
11.19	.08	11.15	5	62
11.31	.12	11.25	7	58
11.48	.17	11.40	7	41
11.64	.16	11.56	6	38
11.84	.20	11.74	6	30

20 ml of distillate containing acetic and formic acids

Burette readings	ΔB	$B+\frac{\Delta B}{2}$	ΔE	$\frac{\Delta E}{\Delta B}$
ml	*ml*	*ml*	*mv*	
[1] 0.20				
3.00	2.80	1.40	29	10
[2] 6.00	3.00	4.50	29	10
9.00	3.00	7.50	23	8
11.00	2.00	10.00	16	8
13.00	2.00	12.00	20	10
	.50	13.25	3	6
	New "zero" observed			
13.50				
13.74	.24	13.62	5	21
13.94	.20	13.84	5	25
14.16	.22	14.05	7	32
14.32	.16	14.24	10	63
14.39	.07	14.36	8	114
14.47	.08	14.43	13	162
14.55	.08	14.51	20	250
14.62	.07	14.59	17	242
14.71	.09	14.67	12	133
14.79	.08	14.75	8	100
14.87	.08	14.83	6	75
14.98	.11	14.93	8	73
15.14	.16	15.06	8	50
15.35	.21	15.25	8	38
15.59	.24	15.47	7	29

[1] Initial readings.
[2] Calculated amount of base equivalent to formic acid=4.20 ml.

The error arising from failure to bring the portion of solution in the shielding tube completely to the end point must be less than $\frac{0.5 \text{ ml}}{\text{ml acid} + \text{ml base}}$ 1 ml, and in these titrations is less than 0.02 ml. Clarke and Wooten [6] have formulated an equation for calculating the end point, but the symmetry of these titration curves seems to justify the estimation of the end point by graphical interpolation. It is also of interest to note that no marked irregularities are seen in the values of $\frac{\Delta E}{\Delta B}$ close to the end point on the alkaline side. It is suggested that the short time required for completing the titration after passing through the end point and the slight excess of base required, when added in small increments, to give a sufficient number of potential readings for plotting the curve on the alkaline side of the end point, explains in part the absence of irregularities in the observations, which might be expected to arise from the behavior of quinhydrone in more alkaline solutions. It is also of interest to note that in the data for the titration of the distillate containing formic and acetic acids no maximum occurs when the amount of base calculated to be equivalent to the formic acid content of the solution is added.

3. EFFECT OF ADDING POTASSIUM CHLORIDE TO SOLUTIONS

It was pointed out above that potassium chloride was added to increase the conductivity of the solutions to be titrated electrometrically. A solution, containing 0.19 g potassium chloride per milliliter, was prepared for this purpose and, since 0.3 ml was found to give sufficient galvanometer sensitivity, this quantity was used in all titrations, except some for which the results are shown in Table 2. The values shown in this table for the amount of base required for titrating acetic-acid solutions, to which varying quantities of potassium chloride solution were added, indicate that the quantity of base required decreases slightly with increasing quantities of potassium chloride. The agreement, however, between the observed and calculated volumes of base, used in titration of dilute solutions of hydrochloric, acetic, and formic acids of known acidities, shown later in Table 3, indicates that any error due to the addition of 0.3 ml of the potassium-chloride solution is small. Furthermore, if the base is standardized with solutions of the acids found in the distillates, any error due to potassium chloride should be compensated.

[6] See footnote 3, p. 172.

TABLE 2.—*Effect of varying quantities of potassium-chloride solution in titrations of acetic acid*

[Solution containing 0.19 g potassium chloride per milliliter]

Acetic acid		Amount of potassium chloride solution added	Base required for titration	
Amount	Normality		Approximate normality	Amount
ml		*ml*		*ml*
		0.3	0.002	11.91
				11.98
				11.84
				Mean 11.91
10	0.002383	3.0	.002	11.64
				11.77
				11.68
				11.77
				Mean 11.72
		.3	.004	12.83
				12.82
				12.87
				Mean 12.84
20	.002479	1.5	.004	12.83
				12.77
				Mean 12.80
		3.0	.004	12.66
				12.79
				Mean 12.73

TABLE 3.—*Electrometric titrations*

[Comparison of observed and calculated volume ratios]

Acid			Base required for titration		Volume ratios			
Formula	Amount	Normality	Approximate normality	Amount	Acids	Observed	Calculated	Deviation observed from calculated
	ml			*ml*				*Per cent*
HCl	20	0.002559	0.004	13.23				
				*13.16				
				Mean 13.20				
CH_3COOH	20	.002479	----------	*12.83	CH_3COOH / HCl	0.973	0.969	0.41
				12.82				
				12.87				
				Mean 12.84				
HCOOH	20	.002047	----------	10.51	CH_3COOH / HCOOH	1.224	1.211	1.06
				*10.47				
				Mean 10.49				
					HCOOH / HCl	0.795	0.800	−0.63

* Titration data given in Table 1.

TABLE 3.—*Electrometric titrations*—Continued

[Comparison of observed and calculated volume ratios]

Acid			Base required for titration		Volume ratios			
Formula	Amount	Normality	Approximate normality	Amount	Acids	Observed	Calculated	Deviation observed from calculated
	ml			*ml*				*Per cent*
HCl	20	.003070	0.005	13.60				
CH_3COOH	20	.002979	---------	13.25 13.20 13.23	CH_3COOH / HCl	0.974	0.970	0.41
				Mean..13.23				
HCOOH	20	.002047	---------	9.18 9.07	CH_3COOH / HCOOH	1.449	1.455	−0.41
				Mean...9.13				
					HCOOH / HCl	0.671	0.667	0.60
HCl	10	.003070	.002	15.15 15.21				
				Mean..15.18				
CH_3COOH	10	.002383	---------	11.91 11.98 11.84	CH_3COOH / HCl	0.785	0.776	1.15
				Mean..11.91				
HCOOH	20	.002047	---------	20.45 20.38	CH_3COOH / HCOOH	1.166	1.165	0.09
				Mean..20.42				
					HCOOH / HCl	0.673	0.667	0.87

4. EXPERIMENAL RESULTS OF TITRATIONS

In Table 3 are given the volumes of base required for the electrometric titration of dilute solutions of hydrochloric, acetic, and formic acids. These solutions were prepared by diluting a known portion of the standard solutions in a volumetric flask. The ratios of the observed volumes of base required for these dilute solutions are compared in the table with the volume ratios calculated from the dilution factors and normalities of the standard acid solutions. Detail titration data are given in Table 1 for the values in Table 3 marked with an asterisk (*) and in the last column the percentage differences between the observed and calculated volume ratios are given.

VI. TITRATION OF DISTILLATES

1. TITRATION OF DISTILLATES FROM SULPHURIC ACID SOLUTIONS CONTAINING ACETIC AND FORMIC ACIDS

In Table 4 the observed volumes of base required for distillates from sulphuric-acid solutions containing known amounts of acetic and formic acids are compared with the calculated volumes. The

latter were calculated from the volumes of base required for titrating dilute solutions of each of these acids of known acidities. Except for the low value observed for experiment No. 3, the observed volume of base required agrees well with the calculated volume.

TABLE 4.—*Comparison of calculated and observed amounts of base required to titrate distillates from sulphuric acid solutions containing known amounts of formic and acetic acids*

Experiment No.	Calculated amount of base required			Observed amount of base required for titration		Deviation of observed from calculated value
	Acetic acid	Formic acid	Total	Approximate normality	Amount	
	ml	*ml*	*ml*		*ml*	*Per cent*
1	8.78	2.96	11.74	0.003	11.82	0.7
2	8.78	2.96	11.74		11.58	−1.0
3	4.41	6.05	10.46	.005	10.04	−4.0
4	6.62	2.27	8.89		8.78	−1.2
5	5.29	3.63	8.92		8.97	.6
6	6.62	9.07	15.69		15.75	.4
7	6.62	2.27	8.89		8.91	.0
8	6.43	5.52	11.68	.004	11.62	−.5
9	8.56	1.75	10.31		10.22	−.9
10	10.29	4.20	14.49		*14.33	−1.1
11	10.29	4.20	14.49		14.29	−1.4
Mean						−1.0

* Titration data given in Table 1.

2. TITRATION OF DISTILLATES CONTAINING ACETIC ACID AFTER REMOVAL OF FORMIC ACID

After titrating portions of the distillates containing both acetic and formic acids, experiments were carried out in which the formic acid in portions of the distillates was oxidized by potassium permanganate and, after a second distillation, portions of the second distillates were titrated for acetic acid.

In Table 5 the observed volumes of base required for portions of distillates free from formic acid and containing acetic acid are compared with the volumes of base equivalent to the calculated acetic acid content. Although the percentage differences between the calculated and observed values in this table are larger than in Table 4, the agreement is perhaps satisfactory considering that the quantity of acetic acid in the original samples was about 0.1 per cent, and that a second distillation is involved in obtaining these observed values. The larger quantity of base required than calculated suggests that either the formic acid was not completely oxidized or that traces of the solution in the distilling flask contaminated the distillate. The addition of barium chloride to portions of the distillates acidified with hydrochloric acid did not prove to be entirely satisfactory in testing for such small quantities of sulphate, which if carried over mechanically from the distilling flask as sodium acid sulphate would require an appreciable quantity of base.

TABLE 5.—*Calculated and observed amounts of base required to titrate distillates containing acetic acid after removal of formic acid by oxidation and a second distillation*

Experiment No.	Calculated amount of base required	Observed amount of base required for titration		Deviation of observed from calculated value
		Approximate normality	Amount	
	ml		*ml*	*Per cent*
1	8.78	0.003	9.05	3.1
2	8.78		8.80	.2
3	7.94	.005	8.20	3.3
4	7.94		8.95	12.6
5	12.65	.004	12.92	2.1
6	13.19		13.56	2.8
Mean				4.0

VII. COMPARISON OF PHENOLPHTHALEIN WITH ELECTROMETRIC TITRATIONS

In order that the procedure outlined for distilling the volatile acids from battery electrolytes and separator extracts may be followed by titrating the distillate, using phenolphthalein as an indicator, rather than following the procedure for the electrometric titration, it was of considerable interest to compare some titration values obtained electrometrically with those obtained with phenolphthalein. In Table 6 are given some values obtained for the titration of dilute solutions of acetic and hydrochloric acids, both electrometrically and using phenolphthalein. Since no precautions were taken to protect the acid solutions from carbon dioxide while being titrated with phenolphthalein, and since the equivalence point for the titration of these dilute solutions is perhaps on the acid side of the phenolphthalein range, it is to be expected that a larger quantity of base would be required for the titrations with phenolphthalein than for those carried out electrometrically. If, however, the differences are due partly to indicator error and partly to carbon dioxide, it is to be expected that at least a portion of the errors from these sources would be compensated if distillates of approximately the same acidities were titrated under the same conditions as in standardizing the base.

TABLE 6.—*Comparison of electrometric and phenolphthalein values for titrating dilute solutions of known acidities*

(Base approximately 0.0038 *N*)

Acid			Base required for titration	
Formula	Amount	Normality	Electrometric method	Indicator method
	ml		*ml*	*ml*
HCl	20	0.002559	13.23	13.52
			13.16	
CH_3COOH	20	0.002479	12.83	13.11
			12.82	13.12
			12.87	

TABLE 7.—*Comparison of calculated and observed volumes of base required for phenolphthalein and electrometric titrations of distillates*

Present in distillate	Indicator values			Difference	Electrometric values		
	Calculated	Difference	Observed		Calculated	Difference	Observed
	ml	*Per cent*	*ml*	*Per cent*	*ml*	*Per cent*	*ml*
Acetic and formic acids	12.01	−1.2	11.87	1.6	11.68	−0.5	11.62
	14.79	−2.9	14.36	−.9	14.49	−1.1	14.33
	14.79	−.7	14.68	1.3	14.49	−1.4	14.29
Acetic acid only	13.56	.5	13.63	2.5	13.19	2.8	13.56
Mean		±1.3		±1.6		±1.5	

Accordingly in Table 7 are given the calculated and observed volumes of base required for titrating distillates from sulphuric-acid solutions containing known amounts of acetic and formic acids. The volumes of base required are calculated from the volumes of base given in Table 6 for the electrometric titration of acetic-acid solutions of known acidities, as well as from those given in Table 6 for titrations with phenolphthalein. The percentage deviation of the observed volumes of base required for the phenolphthalein titrations from the calculated volumes are within the experimental error of the distillations shown in Table 5.

It was pointed out above that the volatile organic acid content of the electrolyte of a cell which has been cycled may be considered to be acetic acid. This is probably also true for electrolyte which has stood in contact with active material of the positive plates, for formic acid can be oxidized not only by a charging current, but also by lead peroxide. Experiments in this laboratory show, however, that acetic acid is not oxidized by the active material of the positive plates. For these reasons no serious error would arise in many cases, if with no further attempt to remove the formic acid, the acid of the first distillate from a sample of electrolyte taken from a cell were considered to be acetic.

VIII. SUMMARY

A procedure has been described for the estimation of small quantities (of the order of 0.1 per cent) of volatile organic acids in the electrolyte of lead storage cells and in 30 to 40 per cent sulphuric-acid solutions of wood separator extracts. The volatile acids are distilled after neutralizing about 70 per cent of the sulphuric acid, and portions of the distillates titrated for total acidity. After oxidation of the formic acid in another portion of the distillate, the acetic acid is redistilled and estimated separately.

A modification of a recently described differential potentiometric titration apparatus has been devised and was used in titrating acid solutions of the order of a few thousands normal. It was found to be reliable in estimating the volatile organic acids in the distillates from the sulphuric-acid solutions.

Phenolphthalein titrations were compared with the electrometric titrations of the distillates in order that information might be available regarding the reliability of titrations made with phenolphthalein in such dilute solutions.

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